THE GLASS INDUSTRY

VOLUME 18, NUMBER 5, MAY, 1937

THE ART OF DECORATING GLASS

1: THE SPRAYING PROCESS

By V. H. REMINGTON

B. F. Drakenfeld & Co.

• *Although decorating has become a consideration of foremost importance in the glass industry, little of importance has been written concerning the process. The present series of articles, therefore is a distinct contribution to ceramic literature. Written by a recognized authority, comprehensive in scope, it will prove of the utmost importance not only to the merchandising executive but to the technician actually in charge of the decorating process. The discussion this month deals largely with the spraying of ware. It will be followed by a detailed account of the silk screen and other processes, including patent information and much valuable data.—The Editor.*

During the past few years the volume of glass decorating by all methods has assumed enormous proportions. The modern trend has been to color: glass containers, tableware, and cosmetic jars have all yielded to the artist's inspiration. Inexpensive ware decorated with bright colors has caught the eye of millions, and food packers have not been slow to realize the sales appeal of a useful package studded here and there with bright colored dots and stars. The common milk bottle, whose life at one time averaged only eight or nine trips, now makes many times that number, due in part to a bright, permanent label of vitrifiable enamel. Probably one-third of all milk bottles now made bear the owner's name in color, and, the demand is gradually increasing.

Other articles decorated with glass enamel today include cocktail and highball glasses, tableware, ash trays, vases, lamp bases, glass paneling, advertising signs, and numerous novelties. A few soda bottles are now being labeled with ceramic colors and it is probably only a beginning in the beverage field. It is the opinion of many that the decoration of beer, liquor and soda bottles represents practically an untouched field, and that the day is not far distant when permanent ceramic labels will be universally used in ways of which today we do not dream.

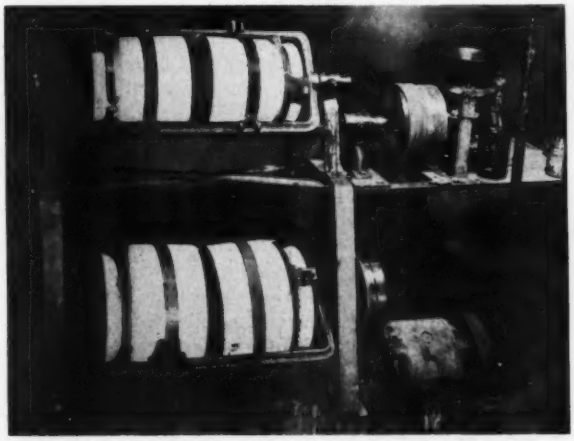
Knowing that little concerning glass decorating processes has been published, it shall be the purpose of this article to present in the language of the layman a few facts concerning the various commonly used methods.

Glass enamels are essentially low fusing, lead borosilicate glasses, to which an oxide or a mineral pigment has been added. After passing through the various processing steps, the finished product is produced as an extremely fine powder. Whether mixed with oils by the color manufacturer, or by the ultimate user, it is this finished powder that is used as a starting point in practically all phases of decorating work.

Although every manufacturer can supply the various enamels ready mixed, it is safe to estimate that better than 90 per cent of all color used is shipped as dry powder. Minimum stocks may thus be kept on hand by the user; for from the same powder, with the addition of suitable oils, paste may be made for printing, banding, or lining. Using turpentine, or alcohol and water, spraying mixtures may be prepared.

I. The Spraying Process

The Vehicle—When color is to be applied to glass by means of a spray gun, the operator has the choice of two principal vehicles: one is turpentine, and the other water and alcohol. Where production speed is the all-important factor, turpentine is the best vehicle for the purpose, since it evaporates rapidly and may be applied to ware that is slightly oily or dirty from handling, without danger of crawling. Eight to 12 ounces of oil of copaiba should be added to each gallon of turpentine to assure a smooth, uniform application. The color will set better to the glass and less of it will be lost in the overspray.



• *A battery of ball mills for grinding and mixing dry paint.*

The amount of turpentine required per pound of dry color is variable and depends upon the nature of the powder, air pressure, atmospheric conditions, and speed of the operation. Under average conditions, one pound of color will require four to four and a half ounces of the turpentine-oil of copaiba vehicle to produce a spray mixture of the proper consistency. Although slightly more difficult to handle, a naphtha cut can be substituted for turpentine. Most oil refineries produce it, and it sells for about one-fourth the price of turpentine.

A vehicle consisting of water, alcohol, and glycerine is less expensive than turpentine, and may be used with satisfactory results on clean ware when the sprayer is not pressed for time. The mixture is especially recommended for white enamels since the danger of discolored ware from decomposing oils during firing is entirely eliminated. Water alone could be used, but with alcohol the evaporation of the vehicle is more rapid. Though not entirely necessary, most operators have found that it is well to add 11 ounces of glycerine to each gallon of the alcohol-water mixture to insure smooth application. Also it will aid materially in holding the heavy color in suspension. Denatured alcohol, or any good alcohol anti-freeze is satisfactory. Quite often a white emulsion is precipitated when water is added to the latter, but this is not likely to alter the results in any way. A good working ratio is three or four parts of water to one of alcohol.

When an article is sprayed with color mixed with either of the two previously mentioned vehicles the surface must not be touched again until after firing is complete. The evaporation of the turpentine (or alcohol and water, as the case may be) leaves the color more or less as a deposit of dry powder. Ware so sprayed can be moved from the sprayer to the decorating lehr only by suitable tongs or paddles that do not come in contact with the fresh color. Many times it is physically impossible to make the transfer in this manner without touching the sprayed surface. To do so without marring the unfired color, any one of several hardening agents may be added to the spray vehicle. The addition of 12 to 15 ounces of balsam of copaiba or damar varnish to a gallon of turpentine will cause the color to set hard to the ware in one or two minutes with forced air circulation. Heated air will help, but is seldom necessary.

If water and alcohol is the chosen spraying medium, one may use sugar, gum tragacanth, or gum arabic as the setting agent. Whichever is used should be first dissolved in water and then added to mixed color. Generally, gum to the extent of .1 per cent of the weight of color will give good results. A convenient method of handling is to dissolve one ounce, say of gum arabic, in 32 ounces of water, to which a few drops of formaldehyde have been added to prevent fermentation. One ounce of this solution will usually be sufficient for 30 pounds of dry color. The exact amount can only be determined through experimentation because all colors do not behave the same due to their different physical characteristics. Do not use more of the setting agents than is absolutely necessary, because they are all organic compounds that must eventually be burned out of the color, and this is always subject to reduction in the presence of these agents. Often the maturing temperature of the color will be increased from 25 to 50 degrees F. when varnish or gum is used. Since some colors may blister, it is well to recheck temperature, color, and fired results carefully before proceeding too far where setting agents must be employed.

Mixing—All domestic glass enamels sold today have been thoroughly ground by the manufacturer. Therefore, it is necessary to mix them only enough to break up any aggregation of color particles caused in packing and shipping. Ball mills and burr type paint mills are proper equipment for this work. The ball mill is unquestionably the best machine for really thorough mixing but since it is a batch unit of fixed capacity, and more difficult to clean, the paint mill is used almost universally in all decorating shops.

Spray Equipment—Spray ware owes its attractiveness to an even application of color by means of the spray gun. Unlike porcelain or sheet iron, a uniform coating of enamel cannot be applied to glass by dipping. The equipment requirements are not excessive and good work may be done with a simple setup.

The Spray Gun—The spray gun is a pistol-shaped unit constructed to produce a spray of air, liquid and solids in the proper proportions. The enamel may be supplied to it from a cup attached to the gun, through a hose by pressure, or from an overhead tank by gravity. Some guns are wholly of the aspirating type and depend upon a regulated air pressure to vary the flow of enamel. Others are of the needle type. Here the flow of spray is regulated by a single trigger which simultaneously varies nozzle opening and air volume. The latter type of gun has been found quite efficient and is especially recommended for production work.

Where the quantity of ware to be sprayed is small, the gun with cup attached is the simplest method of handling color. For jobs involving continuous rapid production, the mixed color should be supplied to the gun by gravity from an overhead container holding two, three, or four gallons and agitated by an air motor-driven paddle. The use of air alone as the agitating agent should not

● *A small paint mill to mix paint for spraying.*

be considered because air quickly evaporates and oxidizes the suspending vehicle.

Air Pressure—The amount of air pressure necessary for any job depends a great deal upon the viscosity of the color. Normally, between 30 and 40 pounds pressure per square inch will be found satisfactory. Excessive pressure wastes color by increasing the percentage of overspray. It creates excessive mist about the main body of spray and means inefficient operation and poor results. On the other hand, with an insufficient amount of air a rippled and orange peel surface is liable to result from inadequate atomization.

Compressed Air Supply—For producing high-grade finishes, the air supply should be free from oil and moisture. This can be accomplished by placing an oil and moisture separator in the supply line. Some of these are equipped with air regulators thus permitting the air pressure to be adapted to working conditions.

Spraying Machines—The spraying operation requires that the ware be revolved rapidly and production economy, that it be handled in rapid sequence. To this end it is possible to construct a machine that will automatically spray a continuous movement of ware. However, actual experience has shown that with the many sizes and shapes which must be provided for, manual spraying is just as economical, and better in most instances. In this case, the spraying machine need only be a revolving table or continuous chain conveyor on which are placed suitable jigs or spindles to hold the ware. These should be connected with a variable speed motor so as to be made to revolve if necessary up to 200-250 rpm. while passing before the sprayer. If the ware revolves too slowly, it will be difficult to spray without showing spiral effects in the applied coating.

Spraying the Enamel—When it comes to handling a spray gun no amount of written description can take the place of practical experience. Nevertheless, there are a number of points of importance concerning the operation that the beginner should especially bear in mind.

In the first place, the sprayer should be made comfortable. He should have a stool of proper height when standing becomes tiresome. The illumination of the ware should not be left to chance, and the source of the light should be so placed that there may be advantage in reflection from the decorated ware. The level of the ware should be just slightly lower than the operator's shoulders. In other words, he should not feel that he is "reaching" for the article being sprayed. Many sprayers have also found in the case of continuous operation that a left to right travel of the decorated piece has a tendency to cramp their action less.

The actual application of color from the gun is best begun at the top of the spinning article, and with an even downward motion of the gun, the entire article covered. The downward direction of the gun should not start, however, until a sufficient amount of color has been applied to produce a wet glossy film. When this stage of application is reached, the same glossy effect should be carried down the length of the article being sprayed. When the bottom is reached the job is touched up by retracing the original motion, but more quickly this time. It is best to spray as wet as possible without rippling or producing an orange peel surface effect. A "dry" spray of color producing a dull surface appearance in the course of application should be carefully avoided.

● *Spray booth for small scale production or sample decorating.*

Ware so coated not only requires increased firing temperatures to fuse the color but the resulting surface finish is certain to be rough or sandy. It is best to maintain a distance of 8 or 10 inches between the gun nozzle and ware.

Most spray guns have a nozzle adjustment for either round or flat spray. It is probably best to use a slight modification of the round adjustment on most types of ware.

There are instances, however, such as the spraying of flat sheets, where the flat type spray should be used so that the successive back and forth strokes may be more easily overlapped. The flat spray adjustment uses a large volume of air and it will therefore be necessary to use a greater proportion of liquid in the color mixture to compensate for the faster rate of evaporation. The flat spray is usually more wasteful of color than the round.

Hoods—Every spraying machine or table should be equipped with a well ventilated hood. This should be wide enough and constructed to catch the overspray from the gun when it is used in any normal working position. However, with the best ventilation possible, there are times when color dust is not entirely removed from the air breathed by the sprayer. In such cases, an efficient respirator should be worn. There are a great many types on the market but only those approved by the Bureau of Mines for lead dust should be considered safe.

Reclaimed Color—No matter how carefully an article is sprayed, a fair percentage of color is bound to get past the ware into the hood and stack. By judiciously placing a few baffles in the hood, some of the overspray may be collected for reuse if it is clean. Ofttimes after it has been screened, a 10 to 15 per cent addition of the reclaimed material may be mixed with fresh color and successfully used, especially if it is a dark color. However, one should watch that blistering does not result because of contamination. If a good many thousand pounds of any single color are to be sprayed a bag house attached to the exhaust system will soon pay for itself.

Checking—Even with experienced sprayers it is necessary to regularly check the amount of enamel that is being applied. This procedure is especially important when the lighter shades of enamels are used because a heavily coated article will look much darker after firing than a thinly sprayed piece. A balance sensitive enough to weigh down to a tenth of a gram should be used.

Weigh a freshly sprayed piece, then wipe it clean and reweigh. The difference in weight is the amount of color applied. Once the proper amount has been decided upon, frequent weighings will materially aid the sprayer in maintaining uniformity.

Enamel Defects—In handling any spray job, cleanliness in all phases of the operation is very important. Clean ware, a filtered air supply, and careful firing go far towards guaranteeing good results. However, it is unreasonable to believe that now and then troubles will not be encountered. That some of its sources may be more quickly recognized a number of possible experiences are here listed:

1. *Blistering*—This is one of the most common defects with sprayed colors. Blistering may be caused by dust, lint, oil or moisture on the ware; by oil or rust in the air supply, or by allowing sprayed ware to become dusty before firing. If varnish is used in the vehicle, too rapid firing may provoke trouble, especially where the color may have been applied heavily. If an oil is not completely volatilized or if carbonization has taken place before the enamel has begun to fuse, trouble in the form of fine bubbles may be expected. Blistering may be the direct result of an overfired color. Some enamel pigments are liable to undergo slight decomposition if overheated or fired for too long a period. Occasionally it may be necessary to spray an article that has been decorated in a previous operation with a printed color or one sprayed on. The object being to make one firing do for both colors. Usually better results will be secured if the harder color is applied first, and if printed, a thin application is best.

2. *Reduction*—Frequently light colors, white enamels in particular, come through the lehr or out of the kiln with a gray cast. Closer examination may reveal either a general grayness or surface covered with millions of infinitesimally small black spots. This condition is usually the result of some form of reduction of the lead in the enamel. It may be caused by non-volatile oils in the vehicle or reducing conditions in the firebox. A slower temperature rise will usually correct the first condition and an oxidizing flame or better lehr ventilation the latter.

3. *Crawling*—Occasionally sprayed ware will be found that has one or more spots from which the enamel seems to have pulled away leaving the glass entirely bare. These spots may vary anywhere from one-sixteenth to a half-inch in diameter, though one-eighth to one-quarter is average. This condition of crawling is common to color sprayed with water or water and alcohol. It is usually due to a film of oil or grease on the ware caused by careless handling. Most any foreign substance on the glass may provoke this trouble. Where water and alcohol is used it is good practice to handle the ware with canvas gloves from the time it leaves the annealing lehr until it reaches the srayer. If moisture from any source is allowed to drop on sprayed ware before it is fired, crawling is sure to result. Sweating kilns are often bad offenders.

Sometimes crawling results from the use of color that has been too finely ground. This may originate with the color manufacturer or in the grinding room of the decorating shop. Some shops are in the habit of grinding for long periods of time, in ball mills, color that is to be used for spraying. A thorough mixing, not grinding, is all that should be attempted. It is impossible to overgrind with a burr type mill.

4. *Sweating*—During the winter months sweating of the ware is often a source of trouble. It is usually caused by bringing glass from a cold wareroom into a warm decorating shop. Printed color will not adhere to ware in this condition. Sprayed color is likely to fire improperly.

5. *Crazing*—Crazing is likely to result if an enamel be applied to glass whose coefficient of expansion is materially different because of the difference in the rate of contraction of the two materials—glass and enamel. Upon cooling if both contract the same amount all well and good, but if one (usually the enamel) contracts more than the other a strain is set up in the ware sometimes great enough (for all oversprayed articles, that is) to literally pull it apart or break it. At least, a strain is set up so that the ware is far more sensitive to mechanical and heat shock. In moderate cases, crazing is characterized by fine hair-like cracks in the enamel faintly visible to the naked eye but may, in extreme conditions, result in the enamel actually peeling off. If the degree of crazing is moderately severe, the reverse side of the glass will present a silvery and perhaps slight iridescent appearance.

Most glass enamels are formulated to fit the ordinary soda lime glass, which has a coefficient of approximately 0.000009. However, it has been found that even though the coefficient of the glass is slightly greater or less than the enamel a moderate coating of color will not craze, at least not enough to cause trouble. Transparent or heavily applied opaque enamels craze the easiest. The lead chromate tomato reds are especially troublesome. Most heat-resisting ware has a low coefficient and special enamels are necessary for decorating it. Very soft high lead content enamels in the past have been frequent offenders but most progressive shops are turning to the more durable less basic colors even though it is necessary to fire a little harder.

GLASS PLANT PROPOSED FOR EGYPT

American capital and American glass companies will be interested in hearing of a project to build a glass plant in Egypt. The plan is to erect a glass works capable of supplying one-half of the present Egyptian importation of window and special glass, such as frosted and opaque glass, which totals more than 8,000 metric tons per year. Eventually, however, the plant will be expanded to provide for the entire needs of the country.

The Egyptians are anxious to have both foreign capital and foreign technical experts participate in forming the new company, which is having the joint attention of Government officials and Egyptian capitalists. They apparently wish to use American equipment, as they consider it superior in performance, and it has been suggested that American manufacturers of glass machines and equipment might participate to the extent of exchanging shares against deliveries. As the United States does not at present enjoy any participation in Egyptian imports of glass, the above project might afford an opportunity to share in the business in the future.

Any who might be interested should communicate with the Department of Commercial Inquiries, at the Ministry of Commerce and Industry, Cairo, Egypt.

THE ANNUAL A. C. S. MEETING

Some 1,500 ceramists, the largest attendance on record, attended the thirty-ninth annual meeting of the American Ceramic Society in New York last month. There, amid the beauty and splendor of the Waldorf-Astoria, they spent a delightful week—and one that was most profitable.

The Glass Division has once more enjoyed two solid days of technical sessions; and again, the quality of the papers presented has been such that it can look back with justifiable pride upon the work that has been done, and upon the data and views reported.

These technical sessions are more and more taking on the character of truly scientific symposia, where the problems have been carefully defined and delimited in such a way that the worker contributes something specific to the spearhead of technological advance. To the practical men engaged in production, many of these scientific reports may seem to have very little, if any, direct bearing upon actual glass manufacture. But, to take one group of papers as a specific example, it will be by the laboratory studies on surface tension that we eventually arrive at a better understanding of such matters as the foaming of melts, the difficulty experienced in plaining certain glasses, the production of cleanly moulded ware, and greater facility in carrying out certain finishing operations. We have only to look at some of the more successful glass manufacturing establishments to realize that in the glass industry, as in many others, science has at last overtaken and gone ahead of art, or technic. And the important advances, such as the application of glass to new uses as in engineering material, and developing additional strength in glass by taking advantage of its behavior in a condition of controlled internal strain, must be made by direct translation of the scientific work of the laboratory into production.

The papers again demonstrated that American glass technologists are commendably conservative. We are recognizing, more clearly than ever before, that our greatest present need is a mass of reliable physical data. We are content to devote ourselves to the development and improvement of methods of measurement which shall produce these data, without attempting to go very far in generalization or in the formulation of theories until we are more sure of the experimental values. Perhaps, as the writer has remarked before, we are too timid in this direction. Perhaps we would be stimulated by a little more willingness to risk the promulgation of theories, even though these might need to be revised or discarded comparatively soon. As a comment, and not by any means as an adverse criticism, it is worthy of remark that the only papers in which definitely theortical statements were advanced were those presented by two men of German training.

In its variety, the program was an excellent one. The biography of Le Chatelier gave historical background and stimulation that may always be acquired by hearing of the works of great men. The physical properties of surface tension, elasticity, viscosity, refractive index, expansivity, diffusivity for gases, tensile strength, photoelasticity, thermal endurance, and hardness (whatever that is!) were covered in papers which presented the most advanced picture of our present knowledge on these matters. The chemistry of glass was touched only lightly. The application to new products, in particular textile material, was the subject of only one paper, and this lent a nice note of variety to the program. However, one of the papers on expansion included a very direct demonstration of utility in plant processes.

The fact that the work of our Division has become important in several fields of engineering, and that it has gained direct recognition from the Society for Testing Materials, was well brought out in the symposium session on Wednesday afternoon. Internationally, as reported by Dr. Hostetter, we are taking an equal share with the foreign societies in the specific testing problems proposed by the International Commission and growing out of the recent Congress. All in all, we may feel that our Division, in its eighteen years of existence, has arrived at a steady if not brilliant maturity. It is making studies of glass which are interesting for their own sake, and which cannot help to be of real service to the glass industry—to which, it must be remembered, we owe and must continue to owe our very existence.

At the business meeting of the Glass Division, held in New York, March 24, 1937, the following changes in the By-Laws, having been regularly proposed in advance of the meeting, were put to a vote and adopted.

Section 1 (amending present By-Laws on officers). The officers of The Glass Division shall be, a Chairman, a First Vice-Chairman, a Second Vice-Chairman, and a Secretary, each to be elected by ballot at the time of a general convention of the Society.

Section 2, duties of the Vice-Chairmen (new section). The First and Second Vice-Chairmen shall constitute the Division's Committee on Papers and Program.

It is the intention of the Division, in making these changes, to provide for promotion each year of the Second Vice-Chairman to be First Vice-Chairman, and of the First Vice-Chairman to be Chairman. However, in order to eliminate the possibility of retaining incompetent or unwilling officers, this plan has not been made mandatory. As it will undoubtedly be carried out by passive understanding, it will provide for continuity in the executive staff of the Division, and for the acquisition of experience so that when a man comes to the Chairmanship, he will have behind him two years' service in conducting the Division's affairs.

The officers elected at the above business meeting are as follows: Chairman, A. N. Finn, National Bureau of Standards, Washington, D.C.; First Vice-Chairman, Louis C. Roche, Maryland Glass Corporation, Baltimore, Md.; Second Vice-Chairman, N. W. Taylor, Pennsylvania State College, State College, Pa.; Secretary, S. R. Scholes, New York State College of Ceramics, Alfred, N. Y.

Cooperation of The Glass Division with The American Society for Testing Materials will hereafter be more closely carried out with the formation of Committee C-14, under the chairmanship of George W. Morey, Geophysical Laboratory, Washington, D. C.

Turning from the session of the Glass Division to the general proceedings of the Society, the most important matter discussed was the amendment of the Constitution, proposed so that an Institute of Ceramic Engineers—and

other similar vertical classes of membership, when and if desired—might be formed within the Society. Under the amendment, the Society is to be divided into three classes: engineers (the Institute of Ceramic Engineers of the American Ceramic Society), technologists and artists.*

The ultimate purpose is to enhance the status of the ceramic engineer, as developments in the last few years have shown this to be quite necessary. A constantly increasing number of states are requiring the certification of engineers. A ceramic engineer, perhaps wishing to build a glass factory, or to give expert testimony in legal controversies, may have his engineering status challenged, and no machinery exists by which he may establish it. Shall he take the examination of a chemical engineer, which certainly he is not? Or of a civil engineer, which is equally far from the mark? Must he take an examination in every state in which he would like to do business? Obviously there is need of an accrediting body, such as the major engineering schools recognize in the Engineers Council for Professional Development.

Several plans have been advanced to meet this situation. One was to form an independent Institute of Ceramic Engineers. To this there were numerous weighty objections, and it was felt that the interests of all would be better served if the new Institute were kept within the American Ceramic Society. The Society has the vehicle for publishing literature; overhead expense, always considerable, would be smaller; furthermore, there is strength in unity. So it was decided. But because the Constitution makes no provision for an engineering classification, amendment was necessary.

The classes which may now be created have no status as a working force in the organization, other than might be had through their representation on the Board of Trustees. They may devise their own internal structure, elect their own officers, establish grades of membership, etc. They may hold no technical sessions; present no papers.

Because the qualifications of a ceramic engineer never have been accurately defined, considerable speculation exists as to the initial membership of the Institute. Following precedent established by the engineering profession, this will be determined by a temporary organization and this was formed under the authority of the trustees during the closing hours of the convention.

Closely allied with the organization of the Institute of Ceramic Engineers is the development of an educational program, details of which were ably reported by Chairman H. E. White. The education of engineers in the United States is moving forward at a rapid pace, and the ceramic engineer must keep abreast with this trend. To this end some method must be devised of accrediting schools of ceramic engineering. The Educational Committee of the A. C. S. found that the Engineers' Council for Professional Development had been evolving just such a program for general engineering colleges. Contact was made with that organization and definite arrangements to cooperate with and apply that organization's system to ceramic engineering.

Several colleges have already requested a committee of the ECPD and the Educational Committee of the ACS to study their curricula and report on their value for ceramic engineers. The Bulletin of the A. C. S. reports what this Committee believes would be desirable background study for the ceramic engineer:

The Committee does not desire to set up any hard and fast limits on the scope and character of the curriculum or on the relative amounts of time that should be devoted to the several groups of studies which will make up a satisfactory course for instruction in ceramic engineering. The Committee has, however, made a careful analysis of the content of such courses in the more widely recognized curricula. The following distribution of time is typical of courses which produce an effective composite for the instruction of well-prepared graduates from schools offering a four-year undergraduate course in ceramic engineering.

	Per Cent
Mathematics	12
Chemistry	12
Physics	6
Geology and Mineralogy (inc. Petrography)	7
Ceramic Engineering (inc. 4 in Ceramic Design)	20
Other Engineering	18
Cultural Subjects, etc. (English, modern languages, economics, physical education, hygiene, military science, sociology, history, other sciences, and electives)	25

Mechanics and Strength of Materials	5
Mechanical Engineering	2½
Electrical	1½
Mechanical Drawing	5
Fuels and Combustion	1¼
Pyrometry	½
Surveying	1¼
	18

Glass Division Papers

The following are summaries of the papers read at the Glass Division sessions:

1. **Henry Le Chatelier: His Life and Work,** By Alexander Silverman, University of Pittsburgh.

Dr. Silverman, long a personal friend of Le Chatelier, first discussed Le Chatelier's ancestry and showed how it played an important part in determining his scientific career. His education, family and family life were outlined. The extent of Le Chatelier's training was shown in the discussion on the subject matter covered in more than 450 articles which he contributed to various journals, and the books that he wrote. His contributions to both practical and theoretical science were covered, including his inventions, the metallurgical microscope and high-temperature pyrometers. The various honors that Le Chatelier received from governments and institutions were listed, with a bibliography of journal articles.

2. **Effect of Certain Oxide Additions on the Surface Tension of Glass,** by C. W. Parmelee and A. E. Badger, University of Illinois.

The apparatus which was developed by Parmelee, Lyon, and Harman for measuring the surface tension of molten glass is now being used to determine the effect on the surface tension when various oxides are added.

The method is a modification of the maximum bubble pressure method as developed by Jaeger and others, in which a sharp-edged platinum tip is used to form a bubble at the surface of the molten glass.

*The proposal to create a grade of Associate Member was discarded.

Robert B Sosman

Equimolecular quantities of several oxides were successively incorporated in a soda-lime glass and the surface tensions of the homogeneous glasses were determined. A lowering of surface tension was produced by the oxides of sodium, titanium, boron, potassium, lead, chromium, and vanadium, in that order. An increase in surface tension resulted from the presence of the oxides of lithium, cobalt, silicon, calcium, nickel, barium, magnesium, aluminum, zinc, zirconium, magnanese, iron and, at the top of the list, cerium. The surface tensions ranged from the maximum of 320 dynes per cm. for the cerium glass and 240 dynes per cm. for the vanadium glass.

3. **Elastic and Viscous Properties of Several Soda-Silica Glasses in the Annealing Range of Temperature,** by Nelson W. Taylor and Paul S. Dear, Department of Ceramics, The Pennsylvania State College.

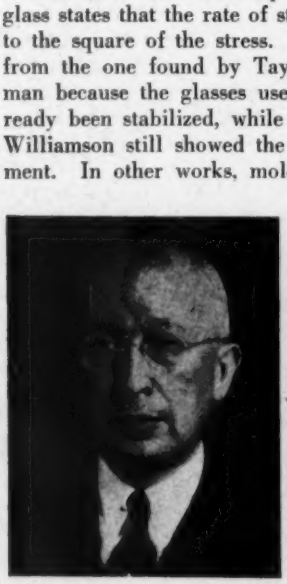
An analysis has been made of the rates of elongation of glass fibers under longitudinal tension. These elongation rates were not constant as would be the case if viscous flow were the only phenomenon occurring, but they were of complex character as if the apparent viscosity were changing with the time. The phenomenon is called elastico-viscous flow and has been described by A. A. Michelson [J. Geology *25* 405 (1917)] although Michelson did not work with stabilized glasses, and he obtained an equation differing from the one given here.

It has been shown by Taylor, McNamara and Sherman (J. Soc. Glass Technology, Feb. 1937), working with a soda-lime-silica glass, in the weight ratio 21:9:70, that the elastic phenomena are completely reversible in character, and are divided in two parts, instantaneous and delayed. The delayed elastic process follows the mathematical relation $dl/dt = kl$ where l is the unstretched length or the distance from equilibrium at any time t, and k is the characteristic rate constant, which measures the fractional change in unstretched length per minute. This is essentially the elastic equation proposed by Clerk Maxwell about 1870 and may be stated as follows: the rate of stress release is proportional to the amount of stress. The well known Adams and Williamson equation for the annealing of glass states that the rate of stress release is proportional to the square of the stress. This empirical law differs from the one found by Taylor, McNamara, and Sherman because the glasses used by these authors had already been stabilized, while those used by Adams and Williamson still showed the effects of prior heat treatment. In other works, molecular rearrangements to a condition characteristic of the temperature of test were still in progress during the strain measurements. Taken together, the first power equation of Taylor, McNamara and Sherman and the second power equation of Adams and Williamson provide very strong support for the contention of H. R. Lillie, W. Weyl and others that for every temperature a glass has a characteristic degree of dissociation, and that in the annealing range and at lower temperatures long times are necessary to stabilize the glass. In fact at room temperature the times are so long, $10^{10} - 10^{100}$ years for commercial glasses, that we may confidently say that no such glass is ever in equilibrium at room temperature.

Taylor and Dear have applied the mathematical analysis used on the soda-lime-silica glass to a series of soda-silica glasses. The simpler chemical system was chosen in order to throw more light on the underlying mechanism. It was possible to get the rate constants for the delayed elastic process and from them the relaxation times, which as defined by Maxwell are the times needed to reduce the unstretched part to $1/e$ of the original amount, e being the base of natural logarithms. This time corresponds to the "half-life" period of radioactive decay. It was shown that the rate constants (k) and the relaxation time (t) were quantitatively related to the absolute temperature (T) in the usual way, that is plots of log k or log t versus $1/T$ were straight lines. The slopes of these lines permit extrapolation to higher or lower temperatures, and also permit the calculation of the activation energy of the delayed elastic process. The magnitude of this quantity is of significance in understanding the fundamental nature of elasticity, but will not be discussed here.

Another point of interest in the present work is that Young's Modulus, based on the total elastic distortion, instantaneous and delayed, appears to be constant and independent of temperature. This was found also by Taylor, Sherman and McNamara in studying the soda-lime-glass. Hitherto, workers have computed Young's Modulus in terms of the instantaneous elongation only, and have found the modulus to diminish as temperature rises.

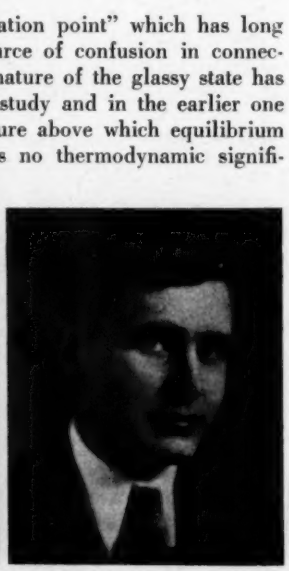
The so-called "transformation point" which has long been a bugaboo and a source of confusion in connection with the study of the nature of the glassy state has been shown in the present study and in the earlier one to be merely that temperature above which equilibrium is rapidly attained. It has no thermodynamic signifi-



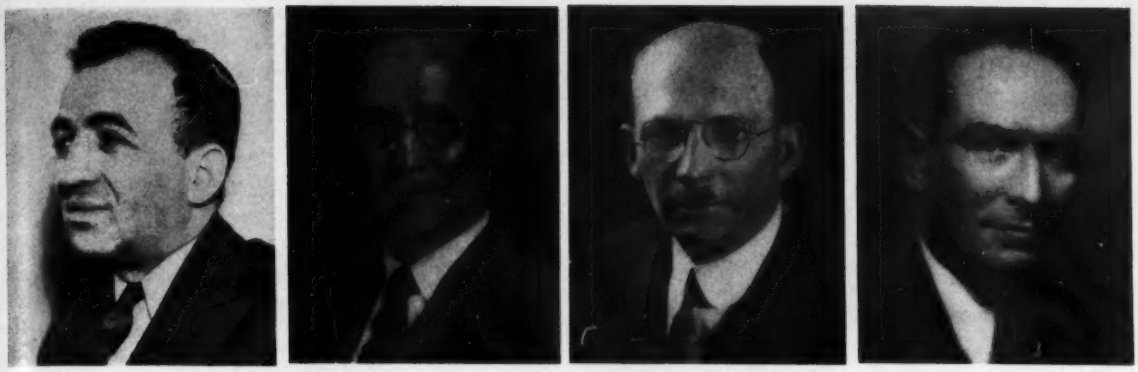
Alexander Silverman

C. W. Parmelee

R. M. King



B. S. Ellefson



J. E. Rosenberg *A. S. Watts* *James Bailey* *A. K. Lyle*

cance. There are no discontinuities in properties between viscous liquid and glass provided the glass is stabilized. If the properties of actual glasses depend on their thermal history or heat treatment it is because some of them are not in equilibrium. It is true that the term "transformation point" has some practical value in indicating roughly the temperature of rapid annealing, but from a strictly scientific standpoint it is meaningless.

Data on the viscosity of the several glasses at various temperatures have been obtained, and a log viscosity versus $1/T$ relation shown to be linear. The range covered was from 10^{11} to 10^{15} poises. The results throw considerable light on the nature of the viscous process but will not be discussed here.

5. **Base Release of Some Commercial Glasses as Determined by Electrodialysis,** by R. M. King, Ohio State University.

Well established methods of electrodialysis were employed in treating various glasses which had previously been tested by Taylor, using the American Ceramic Society No. 1 powder method. Since by this method the base release at one and one-half hour time intervals was determined, curves were plotted showing the rate of release. These curves show that the rate of release is practically constant after three hours. Results for four hours of electrodialysis are higher than those obtained by Taylor with the exception of two glasses treated with sulphuric acid. The error of this method is greater than that of the No. 1 powder method.

6. **The Sessile Drop Method. I. Determination of Surface Tension and Density of Viscous Liquids at High Temperatures,** by Bennett S. Ellefson and Nelson W. Taylor.

Data on surface tension are necessary to calculate absolute values of work of adhesion. The absolute values of surface tension reported by Washburn and Likman on the simple sodium silicate glasses, which were to be used in the "wetting" experiments, have been questioned by Pietenpal, Parmalee and Harman. The apparatus described below Fig. 1 lends itself to a study of surface tension by the sessile drop method. A typical photograph of a glass drop on a graphite surface is shown in Fig. 2. This picture was obtained by utilizing the light, radiating from the drop, as the activator for photographic film. By appropriate measurements, and a utilization of Bashforth and Adams tables, it is possible to calculate the volume. Knowing the weight of the glass at room temperature allows one to obtain the density at high temperature. Combining the density determination with other results from Bashforth and Adams tables, one can calculate the surface tension. A reasonable value for the density lends weight to the reasonableness of the surface tension values since the same measurements were used in calculating each one of these quantities. A reasonable check with densities of sodium silicate glasses, as determined by Washburn and Likman, was obtained, but surface tension values were approximately twice as great. They seem to check in order of magnitude the results as obtained by Parmalee, Harman and Pietenpal.

On the basis of relation between ionic size and surface energy it was shown that an extrapolation of Jaeger's results would lead to a value of surface tension for sodium silicate of about 300-350 dynes.

To calculate the loss due to evaporation of sodium oxide it was necessary to obtain a value of the surface exposed by a sessile drop. A method of calculating this from Bashforth and Adams tables was described.

It was pointed out that the use of Quincke's approximation formula leads to a calculated value of surface tension about one half that obtained by using Bashforth and Adams tables. Data were given for a sodium silicate glass as well as for an enamel frit of complex composition.

The Jaeger method used by Parmalee and Harman was recommended for precision, but doubt was expressed as to its reliability for very viscous liquids — 600 poises or over. The sessile drop, lacking in precision, can be used up to viscosities of about 600 poises.

Data show that it is possible to have a contact angle of 60° to 90° when glass is in contact with platinum in the presence of nitrogen or vacuum; however, the value approaches zero in the presence of oxygen. It was pointed out that the discrepancy in absolute magnitude of Washburn and Likman's results might be due to a lowering of partial pressure of oxygen within their furnace thus yielding a contact angle of 60° which would bring the values of the various methods in agreement.

7. **The Sessile Drop Method. II. The Study of the Nature of Glass Metal Adherence at High Temperatures,** by Bennett S. Ellefson and Nelson W. Taylor.

A review was presented of the derivation connecting the work (W) required to separate a liquid from a solid, the surface tension (T) and the contact angle (A). The resulting equation: $W = T\ (1 + \cos \Theta)$. The sur-

face tension (T) to be used is the one obtained in the previous experiments. The contact angle could be observed directly, or a close approximation made by assuming drop shape to be spherical segment and calculating angle from height and radius at base. The volume calculated on the basis of spherical segment was shown to be too small, yielding values of density too large. This was in accordance with expectations. The work of adhesion of sodium silicate on gold was shown to be 469 ergs per square centimeter at 1000°C regardless of the atmosphere; nitrogen, oxygen or vacuum. Fig. 1 shows a drop of sodium silicate on gold in presence of nitrogen. In the presence of nitrogen or vacuum the work of adhesion of sodium silicate on platinum was calculated to be very close to that on gold—470 ergs per square centimeter. The entrance of oxygen, however, allowed the sodium silicate to spread out on platinum, most likely yielding a zero contact angle. This sodium silicate was brought back to its original shape by applying vacuum, as demonstrated by slides.

Pictures of lithium metaborate, and enamel frit on platinum in nitrogen, vacuum and oxygen showed the lack of wetting in presence of nitrogen and vacuum, but indicated the same spreading in oxygen atmosphere. That the rate of spreading was influenced by viscosity and not by rate of oxide film formation was illustrated by the extremely rapid rate at which the relatively fluid lithium metaborate spread over the platinum.

The work of adhesion on carbon was 9 ergs per square centimeter, almost insignificant compared with the work of adhesion of sodium silicate on gold or platinum. even in vacuum.

8. **A Simple Method for Comparing the Expansion of Glasses and Its Application to Casing Glass,** by J. E. Rosenberg and A. Langerman, O. Hommel Co.

The methods for measuring the coefficient of expansion of glasses involves measuring change of length with change in temperature. The change in length is usually extremely small, so that precision instruments have to be used to make these measurements. Aside from the measurements of the change in length, the temperatures must also be accurately determined. The method outlined in this paper is simple, and will in the hands of untrained men given reproduceable and accurate results. The method presented does not measure directly the change in length, but measures the torque produced by the differential expansion of two materials. The reference material whose expansion is known is enameling iron, and the other is the glass. By measuring the torque produced, it is possible to obtain by simple calculations the total expansion between the critical temperature (lower annealing temperature) and room temperature.

The glass to be measured is ground in a glass mill using 100 parts of glass, one of sodium alginate, 25 of water and 25 of alcohol. The thin paste produced is applied by spraying to the outside only, of a steel cylindrical ring made of enameling iron and covered equally on both sides with ground coat. Between one and two grams of the glass is applied on a ring about 8½ inches in circumference and one inch wide, and the amount used must be known accurately. The glass is melted onto the ring by firing at about 1500 to 1600 for two to three minutes. After firing, the points at which the ring was welded are ground off and the force just necessary to part the ends of the ring is determined. This force for commercial glasses was found to be anywhere between 100 and 500 grams. Since the force can be determined within less than one gram, the accuracy can be quite good. The equation used for calculating the expansion coefficient is:

$$f_m = \frac{t_s + t_g}{r}(\alpha_s - \alpha_g)\ \Delta T\ E_g\ \frac{W}{d}$$

Where f_m is the measured force, t_s and t_g the respective thicknesses of the steel and the glass, r is the radius of the ring, α_s and α_g are respectively the average expansion coefficients between the critical and room temperature (ΔT), E_g modulus of elasticity of the glass, W the weight of glass used and d its density. The equation was checked and found to be accurate by using glasses obtained from the Bureau of Standards on which the data was known.

By means of the ring it is also possible to determine the critical temperature, as at this temperature there would be no force acting on the ring. By measuring the force at various temperatures and extrapolating to the zero force, one obtains a fairly accurate indication of the critical temperature. It was found to be most accurate for lead glasses whose expansion coefficient is the same up to the critical temperature. To be more generally accurate, the change of force with change of temperature should be measured closer to the critical temperature than the 100° C which was used.

Some data was presented on a series of casing glasses. It was shown that in every instance for successful casing of two glasses the one which gave the highest force on the ring test was on the outside. Where trouble was encountered in the plant in casing certain pairs of glasses, it was found that a higher expansion glass (lower force on the ring) was used on the outside. Mathematical expressions were developed, relating the stress in the glasses with their physical properties and the shape of the cased article.

The data indicates that for successful casing:

1. The inside glass should be as thick as possible.
2. The outside glass as thin as possible.
3. The outside glass should have a lower integral expansion than the inside glass in the temperature interval between the critical and room temperature of the glass having the lowest critical temperature.

10. **Some Studies on Reactions between Glasses and Phosphate Solutions,** by J. B. Brown and A. S. Watts, Ohio State University.

The durability of glass when exposed to phosphate solutions was determined in the following manner: 75 cc. of S4 (a saline solution containing phosphates) was placed in a 125 cc. Pyrex flask. The glass to be tested for durability was fused to a porcelain plate and placed in the solution which was then heated for two days at 80°C. The sample was then removed, washed with hot water, dried, vigorously rubbed with a cloth and then examined under a microscope at 75X for the degree of etching.

From the results of an extended investigation on the reaction between glass and the phosphate solution it was concluded that: 1. phosphate solutions, which are corrosive to glass, become inactive when they are stored in glass for some months, or when they are heated in glass for some hours; 2. the inactivation is accompanied by solution (or peptization) of certain constituents of the

CONVENTION SCENES

1. *The spotlight is on Lowell Thomas.*
2. *A lounge on the Queen Mary.*
3. *The ladies walk the (gang) plank.*
4. *Night Club panorama.*
5. *A good smoke and good food.*

2

1

3

glass, especially sodium, magnesium and silica; 3. the addition of small amounts of sodium silicate to the phosphate solution will also cause inactivation; 4. if water is heated with powdered glass and a phosphate solution made up from this treated water the resulting solution is inactive.

11. **X-Ray Diffraction Studies of Silica and Soda-Silica Glass,** by B. E. Warren and J. Biscoe, Massachusetts Institute of Technology.

Mr. Biscoe has been appointed Glass Research Fellow at M.I.T. and this paper is a first report of work done under the auspices of this fellowship, sponsored by eight members of this society.

During the past year one or two papers have appeared which reaffirm the idea that vitreous silica should be considered as small cristobalite crystallites and that the X-ray patterns of vitreous silica are completely explained from this picture (Valenkov and Poray-Koshitz.) If one wishes to interpret the diffraction pattern of vitreous silica as due to small cristobalite crystallites one can calculate directly from the pattern the average size of the crystallites. It has seemed worth while to make a careful determination of this quantity using the best experimental conditions. Since only the first strong peak at $\frac{\sin\Theta}{\lambda}=0.12$ can be used it is only the small angle part of the pattern which is needed and a flat sample with Cu radiation and large camera gives the best results. Patterns were made by transmission through a thin slab of vitreous silica and a slab of cristobalite powder using a vacuum camera and monochromatic Cu radiation. The microphotometer records were changed into intensity curves in the usual way. The corrected half intensity

4

5

breadth is B = 0.181 radians and putting this value into the Bragg particles size equation one calculates L = 7.7A for the average crystal dimension.

$$L = \frac{0.89\ \lambda}{B \cos \Theta} = \frac{0.89 \times 1.54}{0.181 \times .98} = 7.7A$$

This value is appreciably smaller than the values given by other workers (Randall 15A, V.P.K. 10A), their higher values being due to poorer experimental conditions.

So far the results are straightforward and reasonable, the only remaining question is whether the value 7.7A is compatible with other properties and whether it makes sense to talk about crystallites of this size.

The unit cell of cristobalite is about 7.0A on an edge so that we would have here a crystallite containing just over one unit cell. This brings up several interesting questions. 1. Is there any sense to talking about crystals of the order one unit cell? 2. Are these crystallites discreet units separated from the rest of the material? (a) Fourier plot shows each Si is tetrahedrally surrounded by 4 oxygens. (b) Absence of any small angle scattering shows that there are no discreet groups but that the glass is one continuous uniform assemblage.

It is concluded that the term crystal becomes meaningless for particles so small as to contain only one unit cell. There may well be a small percentage of silica glass in which exact regularity has progressed far enough to call these small regions cristobalite crystallites. The important point is that the X-ray results show conclusively that the predominant part is in a form in which exact regularity extends for too short a distance to allow the term crystal to have any meaning.

A Fourier analysis has been made of a sample of soda-silica glass (26.9 per cent Na_2O). The resulting distribution curve shows that each silicon is surrounded by four oxygens as in vitreous silicon and that each sodium has on the average six oxygen neighbors.

12. **Some Observations on the Relations between Composition and Specific Refractivity of Glass,** by A. N. Finn, National Bureau of Standards.

The specific refractivity R was computed for 60 oxides from the refractive index and density data of more than 400 compounds reported in the International Critical Tables and also for a large number of glasses. It was found that: 1. the R for each oxide is substantially the same as that obtained from data on glass; 2. that when RW (W being the hydrogen equivalent weight of the oxide) is plotted against the ionic radius, r, the oxides divide themselves into two distinct groups, the first group containing members of Groups IA, IIA and IIIA (according to Deming's periodic arrangement), and the second group containing all other oxides. The relation between RW and r for each group may be expressed rather accurately by the two following equations, respectively:

(1) $RW = 2.3 + 2\ (r + r^3)$

(2) $RW = 2.3 + 2\ (r + 3\ r^3)$

The intercept, 2.3, appears to be the cube of the radius of oxygen (1.32). The radii used are Pauling's theoretical radii for most of the ions, or Goldschmidt's "observed radii" where Pauling's are not available. Although the equations given here are derived empirically, their symmetry, as well as the simplicity of the constants, suggests that they may have some basis in theory.

Woldemar Weyl

W. C. Taylor

13. **The Diffusion of Helium and Hydrogen Through Pyrex (chemically-resistant) Glass,** by Nelson W. Taylor, William L. Rast, and Paul L. Smith, Department of Ceramics, The Pennsylvania State College.

A great deal has been written about the influence of heat treatment on the properties of commercial glasses, such as color, strength, viscosity, electric conductivity, etc. It is generally believed that structure changes or molecular rearrangements may occur, but very little detail is known. For many years the nature of the so-called "transformation point" has been a subject for discussion. Professor G. Tammann, of Göttingen, who has been very active in the study of the nature of the vitreous state, has proposed that we regard the condition above the transformation point as a viscous liquid, and below, an amorphous solid. The question has been discussed in detail by E. Berger [J. Am. Cer. Soc. *15* 647 (1932)] who concludes that the "transformation point" really marks a boundary between liquid and glass.

In order to get new evidence on this problem the authors carried on a series of measurements on the diffusion rates of helium and of hydrogen through Pyrex laboratory glass, over a range of temperature and pressure. The diffusion method was used because in the hands of Dr. W. R. Ham of the Department of Physics of the Pennsylvania State College, it has proven very successful in bringing to light the various structure changes in boron and nickel, for it appears that every change which the metal undergoes has a measurable influence on the rate of hydrogen diffusion. This sensitivity of diffusion rate to the structure of the host material probably arises from the intimate interaction of diffusing atoms and host atoms. The phenomenon is essentially "chemical" rather than simple escape of gas molecules through narrow cracks or channels.

In the glass work here described, helium and hydrogen were chosen because they have the most rapid diffusion velocities and they are therefore easily measured by trapping and use of a McLeod gauge. For a glass, Pyrex laboratory glass was chosen because it was easily sealed to the rest of the glass apparatus for handling the gas. The sample consisted of a 5″ Pyrex test tube sealed by a ring-seal into a larger tube and the whole placed in a furnace having automatic temperature control to 0.5°, and temperature uniformity from end to end of 0.25°C. After thoroughly testing for leaks the sample was heated to about 400°C. Measurements of diffusion rate were made over a 3-hour period, with one atmosphere pressure of helium or hydrogen gas on the high pressure side of the sample, and the other side ex-

hausted except when trapped for gas collection. The temperature was raised in steps of 5°-10°. Usually about 3 points were taken each day. When the annealing range (527-553) was reached the log (rate) versus 1/T curve bent gradually upwards to higher rates and became tangent to the curve for the stabilized glass. The highest temperature of test was 590°C. Measurements were taken at successively lower temperatures until 337°C had been reached. Subsequent tests were made up and down this temperature interval five times, with reproducible results. Over the range 590°-442° the log R versus 1/T curve is exactly straight, the individual points deviating less than 0.5 per cent from the line. This interval includes the annealing range 527-553, as well as the "transformation point" (550° from the expansion curve) and shows absolutely no evidence of discontinuity or change of slope. We may therefore conclude that the properties of viscous liquid and stabilized glass are continuous with one another. At about 442° some internal molecular rearrangement in the glass occurs, for the slope of the straight line between 442° and 337° is less than that for the range 590°-442°. Rates for H_2 were roughly 2 per cent of those for He.

14. **Physical Characteristics and Properties of Textile Material Made from Glass,** by John H. Thomas, Owens-Illinois Glass Co.

This will be presented in full in the June issue.

15. **An Attempt to Correlate Some Tensile Strength Measurements of Glass,** by J. Bailey and A. K. Lyle, Bailey & Sharp Co.

Tensile strength measurements on glass have been recorded in the literature in great numbers. The strengths found vary from about 3000 lbs. per square inch in pressure ware to more than one million pounds per square inch in very small fibers. Even ordinary test pieces such as canes and laths give strengths from 6,000 to 20,000 lbs. per square inch. In almost every case, so little data is given that the result cannot be analyzed. Notwithstanding the wide variation in strengths found, the authors showed that the application of a few simple principles based upon the theory of flaws and stress concentration caused by them would enable much of the divergence in the recorded results to be explained.

Recent experiments by L. V. Black and F. W. Preston have demonstrated that the strength of glass is dependent upon the time of application of the load, the former having conducted an extensive series of tests using a wide range of uniformly increasing loads and the latter having used a series of constant loads and timing the breakage. Preston's data permits the time required for breakage at any stress to be determined by plotting his results on logarithmatic paper and drawing a curve through the points. If the time is in seconds then it may be assumed that the reciprocal of the time is the fraction of the breaking effect at that stress for each second. A similar value can be found for every stress. If these values are taken for every 100 lb. stress interval and summed, the result will be approximately the same as if the stress had been uniformly increased at the rate of 100 lbs. per second. When the sum reaches one the glass will break. This method was followed for a wide range of stress intervals and it was shown that the curve thus obtained was approximately parallel to and somewhat stronger than Black's curve when plotted on the same graph. The greater strength of Preston's glass was accounted for by the fact that the diamond cuts were on the compression side of his specimens whereas in the case of Black's specimens one of the cuts was on the tension side.

Black and Preston show that various tests can be compared upon a rate of stress increase basis.

A series of tensile strength measurements of one-quarter inch diameter rods of lime glass was analyzed. It was shown that the results did not make a normal curve of distribution. The average of all values was 11,350 lbs. per square inch, the maximum was 15,818 and the minimum was 6,895. This variation in the strength of individual test pieces was doubtless due to flaws. If the specimens had been tested side by side at the same time in groups and if the loading had been adjusted so as to keep the rate of stress increase the same, all canes in the group would break as soon as the weakest one in the group broke. The result of grouping as above was obtained by combining the individual test results mathematically into all possible combinations of 2, 10 and 50. An equation was derived from these group averages for purposes of extrapolation which permitted the value for any group of rods to be computed. If the strength of a rod depends upon the largest flaw which it contains it is evident that the larger the group the greater are the chances of a very bad flaw being present. If the probability of a bad flaw in one rod is taken as a unit, then the above equation may be considered as representing the flaw probability strength of the group number of canes for which it was computed. This may be considered as an area-strength function in which the stressed area of one test rod is the area unit.

By means of this relation and the strength time or rate of stress relation of Black and Preston, it was shown that strengths varying from 20,000 pounds per square inch to 15,000 pounds per square inch could be obtained in the same glass rods by using a single knife edge load of 4.9 lbs. at the center and varying the span from 1″ to 12″, or a somewhat greater range of strength could be obtained by keeping the stress constant. Similarly it was shown that the measured strength would vary from about 22,000 lbs. per square inch to about 7,500 lbs. per square inch, if the same apparatus were used for all tests but the rod diameter was changed from 1/16″ to 1″ and a loading rate of 9.8 lbs. per minute were used for all sizes.

These computations show the futility of making tests and recording the results unless all details of the apparatus, the dimensions of the test pieces, and the rate of loading are given. They also show that much judgment must be used in comparing the strength obtained on one size specimen with that obtained upon a specimen of another size.

In closing the paper, the authors discussed the possibility of obtaining abnormally high strengths by starting the loading at too great a fraction of the ultimate breaking strength. They also stated that, while their work indicated that corrections such as they devised might be used to compare the strengths of glass obtained by different experimenters in a comparable range, the corrections did not seem to apply directly to either very fine fibers or to bottles, the former being stronger and the latter being weaker than computed values would indicate. The effect of glass composition was not considered.

16. **Effect of Annealing on the Expansivity of Some Glasses,** by J. B. Saunders and A. Q. Tool, National Bureau of Standards.

That portion of the transition range, which is available for experimental heat treatments that are imposed on a glass for the purpose of modifying its physical properties at room temperature, is somewhat broader than the serviceable annealing range on which it centers. To stabilize the glass, at the higher temperatures of the available range for experiment, requires only a few hours at the most, but near its lower limit treatments having a duration of several months may be required. To preserve, during the cooling from treating to room temperature, a condition which properly corresponds to the stabilized condition at the treating temperature consequently requires a very high cooling rate from points near the upper limit, while the rate from points near the lower limit may be quite low. Moreover, in testing the efficacy of the treatments it is often necessary to carry the glass through several cycles in which it is repeatedly stabilized at two or more temperatures.

Under these conditions the effect which heat treatment at different points within this portion of the transition range has on the expansivity was determined for six thermometer glasses. These included the well known borosilicate glass designated by 59^{III} and the remainder appeared to have more or less similar characteristics. The linear expansivities, which were presented at the meeting, were computed from expansion (and contraction) curves which were obtained over the approximate range from 20° to 220°C by the usual interferometric method employed for small samples. In computing the slope (at 100°C, for example) the equation $\frac{dE}{dT} = \frac{d}{dT}(A + BT + CT \log_e T)$, where T is the absolute temperature, was used since this fitted the observed expansions somewhat better than any of the several three-constant equations tested.

The expansivities of the six glasses all decreased as the treating temperatures were reduced. These temperatures ranged from 450° to 630°C, and the expansivity of the 59^{III} sample changed approximately from 5.83×10^{-6} when treated at 475° to 6.22×10^{-6} when treated at 630°C. Changes of about the same order were obtained for the other glasses and the same range. There was a measurable difference between the expansivities of some of the glasses (extreme difference about 0.18×10^{-6}) when they were treated at the same temperatures; but by treating each glass at a properly chosen temperature which differed from that of the others (extreme difference about 70°C), all could be made to have approximately the same expansivity. However, this could be done only for a range of expansivities between slightly less than 5.9×10^{-6} to somewhat about 6.0×10^{-6}.

17. **The Theory of Photoelasticity,** by Hans Mueller, Massachusetts Institute of Technology.

If a piece of glass or a cubic crystal is subjected to mechanical stresses it becomes birefringent. The usual explanation of this effect is as follows: Under the influence of pressure the atoms move closer together in the direction of pressure, and move further apart from each other in the directions perpendicular to the pressure. Hence, if the distribution of the atoms was originally isotropic, the deformation will make it anisotropic. The new distribution resembles somewhat the arrangement of the atoms encountered in crystals with layer lattices (mica). This explanation implies that the origin of forced birefringence is identical with that of natural double refraction encountered in anisotropic crystals.

Although the above argument is unquestionably correct, it does not account for the facts. Measurements have shown that most glasses become negatively birefringent when compressed, i.e., the index of refraction for light polarized parallel to the direction of pressure is larger than for light polarized normal to the strains. In crystals with layer lattices, however, the situation is just reversed. They all show positive birefringence. Hence the displacement of the atoms is obviously not the principal cause of the photoelastic effect.

There exist a few glass types, namely the extra heavy flints ($n > 1.8$) and some crystals (K Cl) which become positively birefringent when compressed. All other physical properties of these glasses and crystals are not markedly different from other glasses or crystals, and hence this reversal of sign cannot be explained by assuming the existence of unusual conditions in these substances. A simple solution of this dilemma can be given by assuming that the photoelastic effect is the result of two causes—one producing positive, the other creating negative birefringence. This hypothesis explains also why glasses can be made which show no photoelastic effect. In these glasses the two effects compensate each other.

Some time ago the writer developed a mathematical theory of photoelasticity based on the above hypothesis (Physics, Vol. 6, p. 179, 1935, and Phys. Rev., Vol. 47, p. 947, 1935). It is assumed that the positive contribution is caused by the displacement of the atoms. This effect can be calculated with the help of a mathematical procedure which is similar to the derivation of the Lorentz-Lorenz equation for refraction. The calculation leads to the result that the positive effect increases rapidly with increasing refractive index. The reversal of sign of the photoelastic constant for glasses of high refractivity can now be understood; it is due to the fact that in these glasses the positive effect is very large and outweighs the negative effect.

By comparing the theoretical value of the positive effect with the measured value of the photoelastic constant it is found that the second, or negative, effect has nearly the same value for all glasses. Since the refraction of glasses is largely due to the oxygen ions in SiO_2 and PbO this result suggests that the negative effect is connected with a specific property of the atoms, or ions. We must assume that a strain produces a slight deformation of the atoms. Modern atom mechanics shows that such deformations of the electron shells are possible, and Fajans and Joos have produced a great deal of evidence showing that the optical properties of the atoms vary if the arrangement of the neighboring atoms is changed.

Due to a compression the atoms are squeezed and are slightly flattened like a rubber ball under pressure. It can readily be understood that this squeezing gives rise to negative birefringence. The deformation of each atom is extremely small, and it does not seem likely that it could be detected with other methods (X-rays, spectroscopy), but due to the large number of atoms the effect is sufficiently large to account for the changes of the refractive index.

The proposed theory has been tested and found to be

quite satisfactory in explaining all existing data on the photoelastic behavior of glasses and cubic crystals. Improvements and refinements of the theory are possible, but they cannot be made until we have a larger amount of more accurate experimental data.

18. **The Strength of Glassware and the Validity of the Gaussian Curve,** by F. W. Preston, Butler, Pa.

Pressure test results obtained on lots containing 1,000 bottles each were plotted and the curve obtained. An analysis of the curves so obtained showed that the normal curve of frequency coincides with the results obtained in the thermal shock and pressure testing of glassware sufficiently that various investigators may calculate their averages, probable errors, and standard deviations as if the curve were rigorously applicable, thus facilitating comparison of their own results with those of others.

It was also shown that the curve as obtained in practice does not fit with such a degree of precision that it can be extrapolated at all beyond the observed limits. It is therefore impossible to estimate how strong or how weak the strongest or weakest bottle out of 100,000 or 1,000,000 bottles will be. Neither theory nor experiment justifies such an extrapolation. In all of the curves obtained experimentally a slight variation was observed. This variation is in the direction that would be expected from theoretical considerations. The curves obtained in the bottle pressure tests showed that bottles and presumably other glass articles are actually somewhat better in practice than the normal curve of frequencies imply.

The fluctuations of strength as indicated by testing to destruction of comparatively large samples of the most homogeneous specimens of bottles available at the present day were described and examined in some detail. The adequacy of various size sample lots was discussed and the fact that even 1,000 bottles is only a sample not necessarily typical of a lot of 10,000 bottles is indicated by the secular drift.

19. **Some Comments on the Constitution of Glass** by W. Weyl, State College, Pa.

In complete agreement with a recent paper of Morey, it was pointed out that our present day knowledge of the constitution of the vitreous state is far from being complete. In comparison with gases and crystals, it is much more difficult to formulate concepts concerning the constitution of liquids in general, and glasses in particular.

Although it is not possible at present to give a rigorous picture of the nature of the vitreous state, it is nevertheless necessary, from a practical viewpoint, to have a working hypothesis in order to deal with such problems as the coloring of glasses, the solubility of gases, the effect of mineralizers, and the distinction between glasses and condensation products.

Taking into account intermolecular forces which give rise to association and dissociation, solvation, etc., it is possible to explain the facts on a common basis. As an example, the expansion behavior of glasses with different heat treatments were shown to be completely compatible with the foregoing concepts. Thus, the total expansion could be resolved into two parts; viz., a purely physical expansion which cannot be frozen in and that due to dissociation-association equilibria which may be frozen in by chilling the glass.

In order to study the chemical reactions which take place in glass, the author has introduced various colored oxides into the melt, these oxides serving as indicators. The absorption spectra of the glasses were then analyzed. The results gave a rather thorough insight into the nature of the pertinent reactions. In the discussion it was pointed out that the results of X-ray investigations lead to a conception of the glassy state which is completely consistent with that presented. The apparent differences in the concepts which have been reported are essentially due to differences in nomenclature.

20. **The Work of the Glass Division and its Relation to the Needs of:**

(a) The Illuminating Engineering Society, by H. H. Blau, Corning Glass Works, Macbeth-Evans Div.

In the absence of Mr. Blau, R. A. Miller gave a summary of the work being conducted by the I.E.S. and called attention to the increasing use of plastics in the illuminating field. Mention was also made of the work conducted by the Joint Committee on Illuminating Glasses representing the Illuminating Engineering Society, the Glass Division of the American Ceramic Society, and the Illuminating Glassware Guild on the "Nomenclature of Illuminating Glasses."

(b) The American Society of Heating and Ventilating Engineers, by R. A. Miller; Pittsburgh Plate Glass Co.

As the new developments in the glass field, glass blocks, glass "wool," multiple glazing and others are directly concerned with heating and ventilating problems the two societies have considerable community of interest. The relationship is of such importance that a joint committee should be formed to study such glass problems that are related to heating, refrigerating and ventilating requirements. The work of the A.S.H. & V.E. research laboratories in Pittsburgh was illustrated and the setup of the organization described. One of the investigations now under way is a study of the heat transfer, including solar radiation, through glass building units and flat glass windows. The above investigation, along with the correlation of data and other research will be of great importance to the glass industry as a whole, and especially to the manufacturers producing transparent or translucent glass for construction.

(c) The American Society for Testing Materials, by W. C. Taylor, Research and Development Dept., Corning Glass Works.

Dr. Taylor gave a resume of the events leading up to the development of the A.S.T.M. Committee on Glass and Glass Products. The scope of the committee is:

R. B. Ladoo

Hans Mueller

to clarify nomenclature, and development of methods for analyzing and testing glass, both as such, and as specific products. The chairman of the committee is G. W. Morey of the Geophysical Laboratory. Other committee members will be selected from producers, consumers and general interests in the near future. By working through this committee, the Glass Division will be able to participate in the formation of both national and international standards. One of the first international standards to be investigated by the Glass Division is that of tensile strength.

22. **What Hardness Is, Or What Hardness Is Not,** by L. B. Tuckerman, National Bureau of Standards.

Dr. Tuckerman's presentation of his paper was quite unusual. Straying from the beaten path followed by most investigators on the subject of hardness, Dr. Tuckerman selected a line of attack designed to debunk the use of the terms "hard" and "soft."

A review of the literature on the subject was given and it was shown that the best that can be expected from various hardness tests is a set of values indicating the tendency of the tested material to withstand the action placed upon it by the test procedure. It was the opinion of the author that it will never be possible to connect such values with a so-called "true" scale of hardness. It was also pointed out that the various hardness tests are useful only for measuring the resistance of the test piece to service conditions.

The paper was concluded with actual illustrations of how the terms "hard" and "soft" are used in connection with various materials of commerce. The materials used as examples ranged from soft and hard sponges to soft water and hard liquor. These illustrations served to bring home the author's statement that the terms "hard" and "soft" have considerable flexibility and are therefore meaningless.

23. **Notes and Suggestions on Tests for Thermal Endurance of Glass,** by James Bailey, Inc., Hamburg, N. Y.

As the results of thermal endurance tests depend upon several factors such as the shape of the sample; the character of the glass surface or surfaces; and the degree of annealing of the glass, tests by different laboratories on a standard article and by a standard method would yield the same answer and have no practical value.

The problem therefore should be broken down into its factors and each participating laboratory should be given one factor for study. Tests should be made on glass, as glass, bottles, and ware other than bottles.

The recommended method to be used for testing the thermal endurance of glass as glass was described. The data to be included with the results was enumerated. If several laboratories are to co-operate in working out corrections, the shape, annealing, and surface factors must also be studied.

The method of testing the thermal endurance of glass in the form of articles other than bottles is briefly as follows: the ware is heated in an air bath until thermal equilibrium is reached and then plunged into ice water. At least three articles are to be listed at each temperature. Tests shall be made at 10°C intervals and the complete curve of breakage reported. Additional data to be reported includes all known facts about the article with particular relation to annealing, packing and shipping, surface defects, finish, etc.

In the case of bottles, both the outside and the filling test should be used and data such as was enumerated in the above test included.

24. **Tests on the Thermal Endurance of Glass,** by S. R. Scholes, New York State College of Ceramics.

When these tests are conducted on specimens in the form of glass rods, it is vitally necessary that the degree of annealing or disannealing of the rods be known, in order that the test may be properly evaluated; that in disannealed or strained rods, larger diameters gave relatively higher thermal endurance; that the character of the fracture when the hot rods are dropped into cold water is likely to be that of a cross-break or spiral in the strained rods, and a longitudinal split in the annealed rods; that it is only in the well annealed specimens that the relationship holds approximately, where the degree of thermal shock which the rods will stand is inversely proportional to the coefficient of expansion of the glass.

For the lime-glass rods tested, it was shown that the disannealed rods withstood more than twice the thermal shock which could be borne by the annealed rods.

ALLIED DIVISIONS

3. **Colloidal Graphite and Its Role in The Ceramic Industry,** by R. Szymanowitz and B. H. Porter, Acheson Colloids Corporation.

In this paper the development of colloidal graphite was traced from the early work of Acheson on the plasticity of clays to the present use of graphited lubricants in industry. Much historical data of general interest was given and the physical properties of colloidal graphite suspensions were discussed in detail.

Because of its lubricating properties and its resistance to oxidation colloidal graphite finds considerable use in high temperature applications (such as glass working) where oil is subject to destruction by either distillation or decomposition. In these instances it is customary to mix the concentrated graphite dispersion with a low viscosity oil that distills off readily without undue decomposition with the result that a residue of pure graphite is left on the lubricated surface.

The application of colloidal graphite lubricants to various glass manufacturing problems was illustrated by actual examples. In the case of glass drawing machines a 10 per cent dispersion by weight of colloidal graphite in mineral oil is being used on the rollers of the "Brevet Fourcault" vertical type machines and successfully withstands the high temperatures encountered. The use of graphited lubricants in bottle forming machines was described and it was shown that its use in the parison molds leads to a perfectly smooth graphoid skin being deposited on the mold surface which materially aids the flow of glass into the mold and helps to eliminate the "washboard" effect on the glass surface. Also, at a later blowing stage, by reason of this graphoid film, the glass is prevented from coming into actual contact with the cast iron molds, thereby reducing the tendency for the glass to stick or drag when the mold is opened to deliver the finished bottle. The amount of colloidal to be used in the lubricant is 0.2 per cent by weight to each gallon of the plain oil.

Colloidal graphite lubricants were also shown to be

useful for lubricating the moving parts of glass machinery, the lubrication of the screw pegs used for threading molded glass insulators, and for the lubrication of the various tools used in the manual working and forming of glass articles.

8. **The Analysis of Feldspar: Determination of Ferric Oxide Parts I and II,** by E. W. Koenig, Consolidated Feldspar Corporation.

Part I: Decomposition of the Sample.

The usual methods for the initial decomposition of feldspar in ferric oxide determinations are quite time consuming and require much personal attention. Where a great many iron determinations are required a method of decomposing the sample which is both rapid and accurate must be used.

After reviewing the literature on the subject the author described a method developed in his laboratory that answers the requirements of speed and accuracy. The method in brief is as follows: Three grams of the 200 mesh feldspar sample are placed in a platinum dish of the "Payne" type and moistened with a few drops of water or alcohol, preferably the latter. Twenty ml. of hydrofluoric acid is added and the sample brought into solution by the application of heat. After solution is complete the solution is transferred with water to a 500 ml. Erlenmeyer flask containing a solution of 10 grams of boric acid, 50 ml. of 1:1 sulphuric acid and 100 ml. of water. The solution is then brought to boiling and the iron oxide determined electrometrically with standard dichromate solution.

Results of determinations made on standard feldspars by both the usual HF, H_2SO_4, pyrosulphate fusion method and by the modified method were given. Excellent agreement between the determined and the true values of iron oxide content were found.

Part II: Application of Titanometry.

While the use of titanous chloride solution as a volumetric method for determining iron oxide has several disadvantages, namely, rapid atmospheric oxidation of the titanous solution, there are several advantages to be gained through its use. A study was therefore made of various methods for protecting the solution from oxidation. A review of the literature was given and the method of preparing and storing the titanous chloride solution described.

Data obtained on the use of the titanometric method in the determination of iron oxide in feldspar showed that it offers definite advantages over the methods commonly employed. The precision and accuracy of the determination is comparable to that of the electrometric method with the advantages of rapidity and low cost of equipment and reagents. The almost complete freedom from the interference of certain factors experienced by other methods is an additional advantage.

13. **Nepheline Syenite,** by R. B. Ladoo, Canadian Nepheline Ltd.

Nepheline syenite is an igneous rock composed of nepheline and potash and soda feldspars. The only deposite of commercial importance is the Blue Mountain deposit near Stoney Lake, north of Lakefield, in the Metheum Township, Ontario, Canada. This deposit and the method of milling were described in detail.

The finished product was shown to contain from 0.045 to 0.06 per cent Fe_2O_3, 24 per cent Al_2O_3, 10 per cent Na_2O and 5 per cent K_2O, the remainder being silica. The use of this product in the ceramic industries is the same as that of feldspar. In the glass industry a comparison between feldspar and nepheline reduces itself to the item of cost per unit of alumina content. An important advantage in the use of nepheline syenite is its action on the fusibility of the batch. Furnace temperatures may be lowered and production increased, both of which result in lowered production costs. An additional point of interest is the iron-alumina ratio. If both feldspar and nepheline syenite contain 0.06 per cent Fe_2O_3 and the same percentage of alumina is used in the finished glass, the iron content of the nepheline syenite is really equivalent to 0.045 per cent Fe_2O_3. This is due to the fact that only ¾ as much nepheline syenite is needed and glasses with lower iron content, or higher alumina content with equal iron, may be produced by replacing feldspar with nepheline syenite.

● *Members of the German Ceramic Society (Deutsche Keramische Gesellschaft) who attended the annual meeting of the A.C.S., and are now visiting various glass and ceramic factories in the United States. This photograph was taken as the S.S. "Hamburg" was nearing New York harbor.*

8. **Mrs. New York Shops for China and Glass,** by Alice Waller King and Catherine Connell.

This paper presented the conclusions arrived at after several weeks investigation into the trend of tableware purchases by the women of New York. The buyers of the China Departments of large stores in New York, Brooklyn and Newark were approached and asked to answer the following three leading questions.

1. Has she definitely in mind what she wants?
2. Does she demand imported ware?
3. What is the strongest factor in deciding her choice?

From the answers to these questions it seems that the average New York woman has only a general idea as to the glassware she wants for her table. Any attractive display by the merchant may easily influence her final decision. The primary determining factor is her own personal taste in both pattern and shape. Graceful, classically simple lines have the most appeal and the trend is to all crystal stemware with floral cuttings, although colored stems are acceptable. Value is, as ever, a determining factor, but the day of the specified price range seems past.

Very few women demand imported ware although they are more familiar with it through the extensive advertising campaigns of the foreign manufacturers. The consensus of opinion of the various dealers seemed to indicate that sales of domestic ware would increase if American manufacturers would publicize their products under trade names as the foreign companies do.

CONVENTION HIGHLIGHTS

Attendance—Registration nearly 1,000. Total number of delegates estimated at 1,500.

President's Reception—Miss Eleanor Bates, harpist, stole the show. Though appearing only twice on the program, her playing was a delight. Victor Larsen's International Choir sang well, and provided an unusual type of program. Several of its selections were outstanding. It was an ideal type of curtain raiser for the annual meeting.

The Ceramic Night Club—Orchids to Robert M. Curts for a novel and scintillating revue that packed the Ball Room and its three huge balconies. Although much was expected of Lowell Thomas, he did not disappoint. Many handsome door prizes were distributed among the ladies.

Ladies' Entertainment—Varied and interesting, and of a type that only a city like New York could make possible. Hight light, hard to select from such things as bridge, radio broadcasts, Radio City, dancing, shopping tours, etc.; but the *Queen Mary* will probably linger longest in the memory. A vote of real appreciation to Mr. and Mrs. Winship.

The Waldorf—The entire Society should be grateful to the New Jersey ceramists for selecting the Waldorf, which probably more than anything else contributed to the success of this glass meeting. Here was efficient service and convention facilities at their finest—and what lovely surroundings! Responsible: Manager Hoenig and his capable lieutenants, Miss Root and Mr. Miller.

Meeting Service—Alfred University renewed the laurels it won at Buffalo. Some twenty-four students took care of the slides, acted as pages and performed too many indispensable services to be recorded. Thanks go to the University and its capable alumnus, Mr. Crawford.

Plant Trips—Perfect arrangements were marred by poor attendance due without doubt to the absence of any program Thursday. The Whitewares bus lost a wheel. The Glass Division trip was cancelled. Moral: These trips should be scheduled for Thursday.

Foreign Delegations—The Society was honored by having as visitors until Tuesday a group of twenty-five distinguished ceramists from Europe. Sixteen were from Germany—Sweden, Denmark and Italy were also represented.

1938 Meeting—At New Orleans, exact date and place yet to be decided. Some objection to the city was raised because of its seeming remoteness, but it is probable that these disadvantages are more fancied than real. There is little time lost in transit, higher fares are offset by lower convention costs, and New Orleans is one of the most delightful of all cities for a late-winter convention.

PENNSYLVANIA BOTTLE CO. RESUMES PRODUCTION

Roy R. Underwood, president, and Leslie A. Lummis, who has acquired a substantial interest in the Pennsylvania Bottle Co. and become its vice-president, announce that the Sheffield, Pa., plant will resume operation shortly.

The plant, a modern fireproof concrete and steel structure formerly manufacturing milk bottles, is being equipped with Hartford-Empire feeders, automatic lift-overs and steel lehrs, Lynch "10" machines making ware from fractional ounce up to and including quarts, both narrow and wide mouth, and Miller "JP" press and blow machines making wide mouth and semi-wide mouth jars of all types.

Output will be distributed exclusively through Lummis Glass Co., Woolworth Building, New York, the bottles and jars being lettered with the insignia "LP" interlocked in a keystone to denote the close relationship between Lummis Glass Co., the selling organization, and Pennsylvania Bottle Co., the manufacturing organization.

WEYL TO LECTURE AT URBANA

Dr. Woldemar Weyl will deliver a series of four lectures at Urbana under the auspices of the Department of Ceramic Engineering of the University of Illinois, on May 13, 14, and 15. These lectures will be concerned with the research work done by Dr. Weyl at the Kaiser-Wilhelm-Institut für Silikatforschung in Berlin, and will cover both the theoretical and practical aspects of glass-making. Ample opportunities for discussion of specific problems with Dr. Weyl will be available.

The four lectures will be respectively titled: 1. "The Constitution of Glass"; 2. "The Absorption Spectra of Solutions and Glasses; A Tool for Investigating Intermolecular Forces and Constitution Problems"; 3. "Colored Glasses"; and 4. "The Interaction Between Gases and Molten Silicates."

G. C. A. MEETING, MAY 20-21

The Glass Container Association will meet May 20-21, at the Greenbriar Hotel, White Sulphur Springs, W. Va. A board meeting will be held at the Association's New York headquarters on April 28 to decide on a program.

THE CHEMISTRY OF COLORED GLASS[1]: III

By DR. ING. WOLDEMAR WEYL[2]

• *This is the third and final instalment of Dr. Weyl's interesting paper on the chemistry of colored glasses. In* THE GLASS INDUSTRY *for March, the author discussed the origin of the absorption spectrum and its changes under the influence of the solvent, as well as the dissociation-association equilibria between coloring complexes. In April, the paper dealt with several important oxides and their oxidation-reduction equilibria. By way of conclusion, Dr. Weyl this month deals with the mutual interaction of coloring oxides of different valencies among each other and with the oxides of arsenic. Dr. Weyl will also discuss the possibilities of developing new colors.*

3. Mutual Interaction of Coloring Oxides of Different Valencies Among Each Other and with the Oxides of Arsenic

A description of the oxidation-reduction equilibria in the last section showed clearly the superiority of optical methods of investigation as compared with analytical chemical methods. Nevertheless, in the past, attempts have been made to study these equilibria analytically. In order to simplify the problem, water-soluble alkali silicate glasses have often been used, but it must be remembered that such a change in the composition of the glass is of primary influence in determining the position of the oxidation-reduction equilibrium. Therefore the results of these investigations cannot be used for technical glasses unless utmost caution is exercised. Furthermore, it may be pointed out that only those glasses which contain only one oxide of variable valence could be studied by analytical means. However, from the practical viewpoint, glasses which contain two or more of these oxides are of most interest. Also many glasses contain an appreciable amount of arsenic, and from previous investigations it is known that the trivalent as well as the pentavalent form may exist in glass. In this section an example will be given which forms the basis for the process of decolorizing glass with manganese.

Iron-manganese glasses—In the investigation of iron-manganese glasses, it was necessary to extend the measurement of the absorption into the infra red, for in this region there is an absorption maximum of iron glasses, the height of which could be used to determine the amount of FeO present. This investigation has been carried out in collaboration with Professor W. E. S. Turner of Sheffield. A series of seven glasses, designated A, B, C, . . . G, has been studied. Each glass contains 68 per cent by weight of SiO_2, 10 per cent of CaO, 2 per cent of Fe_2O_3, and 2 per cent of Al_2O_3. In addition, they contain varying amounts of MnO and Na_2O as follows:

Glass	A	B	C	D	E	F	G
% MnO	...	0.5	1	2	3	4	5
% Na_2O	18.0	17.5	17	16	15	14	13

The effect of varying the composition on the absorption spectrum can be seen in curves A . . . G of Fig. 21. Base glass A contains ferrous oxide as well as ferric oxide. The maximum of transparency is at 550 $m\mu$, and this gives rise to a green color. The chemical analysis showed 0.32 per cent FeO and 1.78 per cent Fe_2O_3 present in the glass. The ferrous oxide which arises by thermal dissociation of the ferric oxide which is introduced is responsible for the absorption in the red and infra red. By adding managanese in the form of pyrolusite (MnO_2), a shift of the ferrous-ferric equilibrium toward ferric takes place. This can be seen by the fact that the intensity of the infra red absorption decreases whereas the absorption in the short wave length region is increased. Hence the effect of adding pyrolusite is mainly that of shifting the iron equilibrium towards the ferric side. The color of divalent manganese in the concentrations in which it exists in the glasses A . . . G is too faint to be observed. The deeper color of Mn_2O_3 cannot occur as long as ferrous oxide is present in the glass.

Iron-cerium glasses—The foregoing investigation shows that the effect of MnO_2 as a decolorizer is primarily due to its ability to oxidize ferrous iron to ferric. Cerium dioxide, which has become more and more important as a decolorizer in recent years, was studied in just the same way. Fig. 22 shows the effect of increasing amounts of CeO_2. This oxide acts in the same manner as MnO_2, i.e., it shifts the iron equilibrium toward ferric oxide.

The role of arsenic as an oxidation and reduction

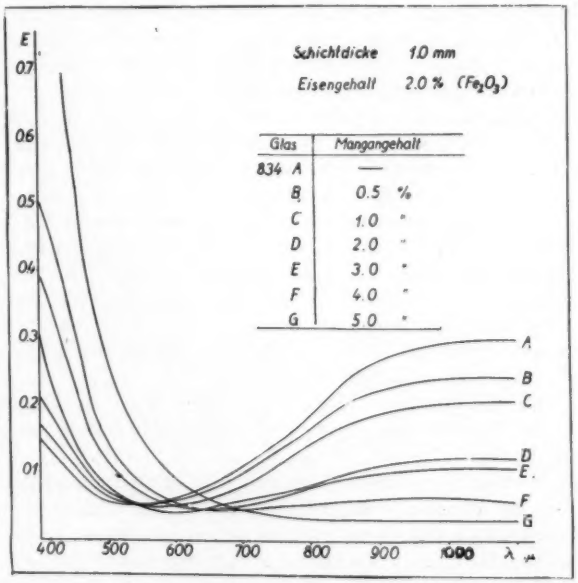
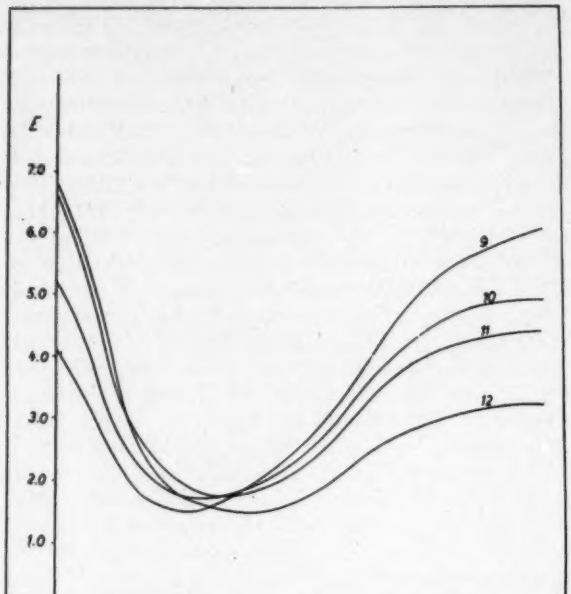


Fig. 21. Absorption of iron-manganese glasses. (From W. E. S. Turner and W. Weyl.) The thickness of the glass is 1.0 mm. and the iron content (Fe_2O_3) is 2.0 per cent. Line A shows the absorption with zero per cent manganese, B with 0.5 per cent, C with 1.0 per cent, D with 2.0 per cent, E with 3.0 per cent, F with 4.0 per cent and G with 5.0 per cent manganese.

[1] A comprehensive bibliography concerning the mechanism of color formation, was published by F. H. Norton, THE GLASS INDUSTRY, Feb., 1935.
[2] Head of the Dept. of Glass Research, K.W.I. für Silikatforschung, Berlin-Dahlem. For the year 1936-1937, Associate Professor of Ceramics, The Pennsylvania State College.

Fig. 22. Iron-cerium glasses. (Thickness, 10 mm., and iron content (Fe_2O_3) 5 per cent.) Curve No. 9 indicates zero per cent cerium dioxide, No. 10 indicates 2 per cent, No. 11 indicates 4.0 per cent and No. 12 indicates 6.25 per cent cerium dioxide.



agent—The effect of arsenic on glass colors has always been a problem of particular interest. One reason for this is that arsenic is added to most glass batches as a refining agent. Another reason is that until the present investigation no satisfactory explanation had been given for the effect of arsenic on colorants and their equilibria. Nevertheless, there exist numerous observations dealing with the behavior of arsenic. However, the general interpretation seems to be ambiguous. Some investigators have emphasized the oxidizing power of arsenic, whereas others have pointed out its role as a reducing agent.

In discussing the color of chromium glasses, it has been mentioned that the addition of arsenic to the batch provides a means of removing the chromate which may be present, thereby obtaining a pure chromic oxide glass. It must be emphasized that it is immaterial whether the arsenic is added in the form of the trivalent or the pentavalent oxide. Recently the author and his collaborators have studied the behavior of arsenic and its compounds in the batch. During glass melting, it was observed that the As_2O_3 first forms As_2O_5, the latter decomposing at higher temperatures. The oxidation of As_2O_3 may be caused by the nitrate or in the presence of sodium carbonate, it may even be caused by the oxygen of the air.

In order to understand the behavior of arsenic and of ions in different valence states in general, it must be remembered that under normal melting conditions some oxides occur only as unstable compounds. Thus, repeated melting causes iron glasses to become richer in ferrous oxide, the ferric oxide consequently being diminished as time goes on. Manganese and chromate colors behave in the same way. As_2O_5, Fe_2O_3, Mn_2O_3, and CrO_3 are unstable in glasses, and they tend to form the more stables oxides of the lower valence states. The oxidizing power of each of these oxides is greater, the more unstable the oxide under the given circumstances.

The difficulty of the whole problem consists in establishing an absolute measure of the stability or instability of a given oxide, and in the fact that the stability is affected by many factors. The oxidation potential of an oxide depends, among other things, upon its concentration, the temperature, and upon the composition of the melt.

The optical investigations, as they have been described for the iron-manganese glasses and the iron-cerium glasses, at least enable us to give a relative measure of the stability and to establish the following series of relative stabilities:

$$\begin{array}{ccc} CrO_3 & \text{———} & Cr_2O_3 \\ Mn_2O_3 & \text{———} & MnO \\ CeO_2 & \text{———} & Ce_2O_3 \\ As_2O_5 & \text{———} & As_2O_3 \\ Sb_2O_5 & \text{———} & Sb_2O_3 \\ Fe_2O_3 & \text{———} & FeO \end{array}$$

This series is arranged so that any oxide in the higher valence state will tend to oxidize any of the oxides in the lower valence states which are given below it. Thus it is seen that CrO_3, being the oxide at the top of the list, has the greatest tendency to split off oxygen and to form the trivalent oxide. Chromates, therefore, are the strongest oxidizing agents and are able to oxidize MnO to Mn_2O_3, FeO to Fe_2O_3 and As_2O_3 to As_2O_5. With respect to FeO, all other oxides in the above series act as oxidizing agents. From the intermediate position of the As_2O_5-As_2O_3 couple, it is not surprising that under certain conditions (e.g., with respect to FeO), As_2O_5 acts as an oxidizing agent, whereas under other conditions (e.g., in the presence of Mn_2O_3), As_2O_3 acts as a reducing agent, forming MnO and As_2O_5.

The validity of the foregoing series is limited. Pronounced changes in the glass composition, concentration of the oxide in question, and temperature may cause an interchange in the relative position of two couples. Thus, in the case of manganese-cerium glasses, it was shown that when 1 to 5 per cent of each oxide is present, Ce_2O_3 reduces Mn_2O_3, as would be predicted. However, at lower concentrations, the opposite effect is found; the addition of cerium dioxide to a manganese glass favors the Mn_2O_3 formation.

As an example of the reducing action of arsenic, Fig. 23 shows the diminution in color intensity of a manganese glass by the addition of As_2O_3. The same effect is caused by the addition of As_2O_5. Fig. 24 shows the oxidizing action of As_2O_3 on the ferrous-ferric equilibrium. The addition of arsenic compounds causes a decrease in the infra red absorption due to the oxidation of ferrous oxide to ferric. The set of curves is very similar to that of Fig. 21.

Changes of glass colors during annealing—The rate at which coloring oxides in different valence states react in glass decreases rapidly with decreasing temperature and increasing viscosity. It is therefore possible to "freeze in" equilibria which are stable in the melt at high temperatures and unstable at low temperatures. As an example, the behavior of copper glasses may be recalled. Under reducing conditions, copper forms cuprous silicates in the melt. Although these compounds are stable

only at high temperatures, they may be obtained at low temperatures by chilling the glass. Slow cooling or reheating to the softening range causes the cuprous compounds to decompose into metallic copper and cupric compounds. Similar reactions take place in glasses where the color is made by "striking."

A typical example is offered by the yellow cadmium sulfide glass. If cadmium sulfide is dissolved in the glass, and either by melting under reducing conditions or by the addition of reducing agents its oxidation is prevented, the color strikes if the glass is tempered in the softening range. At low concentrations, the yellow color of the glass is due to the formation of cadmium sulfide molecules. As the concentration increases beyond the saturation limit, the glass may become opaque due to the precipitation of cadmium sulfide in the form of hexagonal plates (greenokite). On the other hand, chilled glasses containing cadmium sulfide do not show the yellow color. This may perhaps be due to the dissociation of cadmium sulfide molecules into the colorless cadmium ions and sulfide ions. A more probable reason, however, is that at higher temperatures sodium sulfide and cadmium silicate are formed as the stable compounds during the melting period, and that by rapid cooling, the metathetical reaction to form cadmium sulfide and sodium silicate is prevented.

The formation of the selenium ruby glass is analogous to the cadmium sulfide case just discussed. The main constituent of these selenium ruby glasses is cadmium selenide. In a study of the selenium glasses W. Höfler postulates the presence of an alkali selenide, at the same time emphasizing its low stability. It is well known that the formation of ruby glasses is favored by the addition of zinc oxide. This is due to the formation of zinc selenide in preference to sodium selenide at high temperatures in the melt. With decreasing temperature the zinc selenide may react with cadmium silicate to form the ruby colored cadmium selenide.

The foregoing discussion has dealt with those reactions which were purposely carried out and which take place with decreasing temperature. Sometimes, however, reactions occur which are not intended, and which cause a discoloring effect during annealing.

Selenium is doubtlessly one of the most widely used decolorizing agents for glass. The pink color of a glass in which elementary selenium is dissolved is especially suitable for neutralizing the greenish iron color to a grayish tint. Such a glass contains only a part of the selenium in the elementary form, the remainder probably being present as a selenite. Oxidation-reduction reactions may therefore influence the intensity of the pink color.

H. Löffler has recently published some observations concerning the development of the pink color in the lehr if the decolorizing glass contains cerium and arsenic compounds. The reason for this may be as follows:

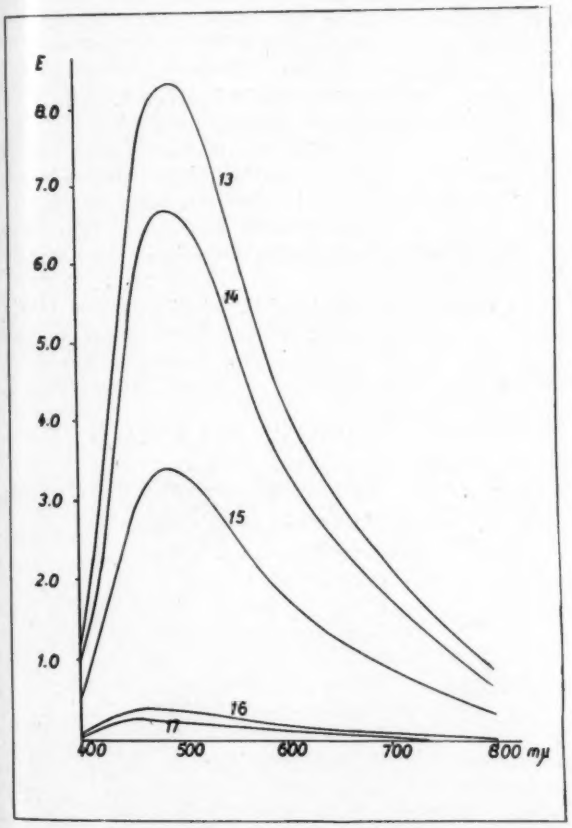


Fig. 23. Manganese-arsenic glasses. (Thickness, 10 mm., manganese content (MnO_2) 2.5 per cent.) Curve No. 13 indicates zero per cent arsenic trioxide, Curve No. 14 indicates 0.5 per cent, No. 15 indicates 1.0 per cent, No. 16 indicates 2.0 per cent and No. 17 indicates 4.0 per cent arsenic trioxide.

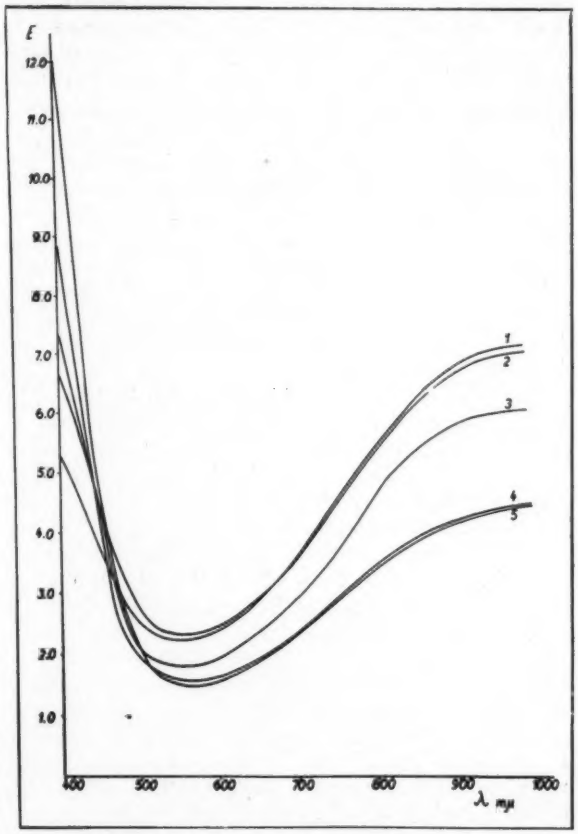


Fig. 24. Iron-arsenic glasses. (Thickness 10 mm., iron content (Fe_2O_3) 5 per cent.) Curve No. 1 indicates zero per cent arsenic trioxide, No. 2 indicates 1.0 per cent, No. 3 indicates 2.0 per cent, No. 4 indicates 4.0 per cent and No. 5 indicates 8.0 per cent arsenic trioxide.

CeO_2 which is added to the batch is reduced to silicates of trivalent cerium with the evolution of oxygen. These cerous compounds tend to be reoxidized at lower temperatures if the necessary oxygen is available; in other words, these compounds act as reducing agents. It is therefore possible that cerous compounds are able to reduce some of the sodium selenite which may be present in the glass to elementary selenium. This would cause the coloring of glassware in the lehr. Trivalent arsenic as well as trivalent cerium may also effect the reduction.

H. Löffler also pointed out that this unwanted coloring effect may be avoided by adding small amounts of antimony to the batch. By doing this, any trivalent cerium which is present is oxidized by the Sb_2O_5 instead of by the selenite, and hence the selenium-selenite equilibrium remains undisturbed.

Discoloring by light—The phenomenon of solarization in glass is closely related to the discoloring effect. Solarization of a glass may be defined as the change in spectral transmission when the glass is continuously exposed to the radiation of the sun. In particular it is known that glass which is transparent to the ultra violet gradually loses this valuable property when exposed to sunlight. Numerous cases of this kind have been discussed in literature on glass.

In the latter case it is fairly certain that the glass loses its ability to transmit in the ultraviolet because of the oxidation of the ferrous oxide to ferric oxide. Ferric oxide has a strong absorption in the ultraviolet. In general, however, very little is known about the detailed changes which take place in glass when exposed to light.

The following considerations will be limited to those photochemical reactions in glass which take place under the influence of sunlight or ultraviolet light, for these are of greatest interest to the glass industry. These effects are not comparable with the more intense effects of x-ray and radioactive radiation and it is therefore not convenient to consider them all together. Cases are known in which photochemical reactions in glass which take place under the influence of x-rays or radioactive radiations may be reversed by visible light. F. Eckert has reported that glasses discolored by x-rays can be bleached by sunlight.

The primary process of light absorption in the visible region consists of an electronic transition in an atom or molecule, the change in energy being proportional to the frequency of light absorbed. An atom or molecule which has thus absorbed light is said to be in an "excited state." The close correlation between optical and chemical properties is due to the fact that both depend upon the outermost electronic shell. Hence, excited atoms, ions, and molecules differ widely in their chemical properties from atoms, ions, and molecules in their normal electronic states. The chemical properties of excited molecules belong to the realm of photochemistry. It is known from studies in this field that many reactions are catalyzed by radiant energy, and that some other reactions which proceed in the dark are completely reversed under the influence of light. The reaction of hydrogen and chlorine in sunlight and the photo-decomposition of silver halides are examples of both types.

Reactions which take place in glass may also be affected by light in these two ways. For example, let us consider the purple coloring of glasses decolorized by pyrolusite in daylight. This purple color is caused by the oxidation of Mn^{++} to Mn^{+++}. From the previously mentioned investigation of iron-manganese glasses, it is known that the reactions between iron and manganese always lead to the formation of MnO and Fe_2O_3 in the melting interval. However, no conclusions can be drawn as to the reaction and stability of these oxides at low temperatures. It is therefore not impossible that at low temperatures the foregoing reaction is reversed, with the formation of ferrous iron and trivalent manganese. Stating this in another way it may be that the reaction

$$2\ MnO + Fe_2O_3 \rightleftarrows Mn_2O_3 + 2\ FeO$$

is shifted toward the right at low temperatures. Such a reaction as the above cannot take place in the cold glass because of the high viscosity and probably high activation energy. However, if additional energy is supplied in the form of light quanta, it may become possible, with the resultant formation of the purple color.

There is another possibility of explaining the above-mentioned purple coloring. Let us assume that MnO and Fe_2O_3 are the stable oxides at low temperatures as well as at high temperatures. This would be true, however, only for ions in their normal states. But ions in metastable states may react in just the opposite way to ions in the normal states, as has already been mentioned.

It is seen that both of the foregoing ideas may account for the phenomenon of discoloring of iron-manganese glasses by sunlight. In the same manner, other types of discoloring such as that of cerium-arsenic glasses can be explained. According to Eckert and Schmidt, the titanium content plays an important role in respect to the light sensitivity of glass. This is worthy of mention inasmuch as titanium is a widely distributed element and is always introduced into glass by the sand.

The decision as to which of these two explanations is the correct one cannot be reached by studying only the discoloring phenomena. It is also necessary to consider the behavior of glasses after the exposure to light. Let us illustrate this by considering the cerium-arsenic glasses as an example.

According to F. Eckert and K. Schmidt, cerium-arsenic glasses become yellowish brown when exposed to daylight or to ultraviolet light. This discoloration is probably due to the formation of tetravalent cerium, according to the equation

$$2Ce_2O_3 + As_2O_5 \rightleftarrows 4CeO_2 + As_2O_3$$

The phenomenon is very dependent upon the concentration of the ions and upon the composition of the base glass. Starting with a glass of the following composition:

Component	Per Cent
SiO_2	66.2
B_2O_3	8.8
Al_2O_3	0.9
CaO	7.9
K_2O	4.1
Na_2O	11.8
As_2O_5	0.3

Eckert and Schmidt have melted glasses with increasing amounts of cerium, the arsenic content being kept constant.

After exposure of these glasses to a quartz-mercury lamp, the glass containing about 2.5 per cent Ce_2O_3 showed the maximum discoloring effect. If the discolored samples are put on a hot plate the discoloration

disappears and in a dark room, a strong phosphorescence can be observed at temperatures as low as 120°C; the process becomes instantaneous at 420°C. Discoloring and regeneration can be repeated indefinitely.

The observation that the reaction causing the discoloring effect is proceeding in the reverse direction in the dark, indicates that the second explanation previously described is correct, namely the reaction between metastable states. Ce_2O_3 and As_2O_5 are the stable oxides at room temperatures as well as at high temperatures. A reaction takes place only when the ions are in the excited states. The chemical reaction of the metastable ions leads to the formation of CeO_2 and As_2O_3. These compounds are unstable in their normal states, and therefore they form Ce_2O_3 and As_2O_5 in the dark, the energy being emitted in the form of radiation (phosphorescence).

The investigation of analogous discoloring effects is also of interest due to the fact that under excited conditions, compounds can be obtained in glass which cannot be obtained by ordinary means. A striking example is the formation of rose-colored vanadium glasses containing divalent vanadium.

It is not necessary to assume that each discoloring phenomenon is due to the interaction between two oxides. Pure arsenic glasses may show a discoloring because of the internal oxidation-reduction of the As_2O_3 into As_2O_5 and metallic arsenic, the latter giving rise to a brownish gray color. This photochemical reaction is not at all limited to arsenic present in glass; it has also been observed for some crystalline arsenic compounds.

A detailed investigation of the photochemistry of glasses would not only be of interest for the elucidation of the constitution of glass, but it would also suggest ways of avoiding this glass defect which is particularly noticeable in places where there is a large amount of sunlight throughout the year.

4. Possibilities of Developing New Colors

In this discussion the various factors which influence glass colors have been elucidated. These are mainly the solvation of the coloring ions, dissociation-association equilibria, and the oxidation-reduction equilibria. These factors are influenced by the conditions of melting, the composition of the base glass, and the heat treatment.

In regard to technical applications, many restrictions are necessary, particularly the possible variations in the base glass. Thus, the pink cobalt color cannot be used technically because its formation requires a base glass which differs rather considerably from a representative one. Another limitation is the composition of the furnace atmosphere. Thus the blue color of the divalent chromium and yellow color of the hexavalent chromium require for their formation more extreme reducing and oxidizing conditions than are ordinarily encountered.

From the standpoint of the glass industry, the actual number of colorants which can be used is greatly limited. Considering this, what can we say about the future development of glass colorants? Unfortunately, there is very little hope for developing new types of ionic colors. However, there are two further possibilities for future research. Concerning the effect of the coordination number, it has already been mentioned that new coloring effects may be obtained for the same ion by introducing it into different lattices. Of course, this method can only be applied to pigment colors for glazes, and enamels; that is, to colorants analogous to the chrome-tin-pink. Studies on these coordination colors in special crystal lattices as host are now in progress in this laboratory.

Another possibility for developing new colorants which has not heretofore been mentioned is based upon the interaction of different coloring ions upon one another. The beautiful yellow color which is obtained by adding both cerium oxide and titanium oxide to a glass is an example. Unfortunately, no satisfactory explanation has yet been offered for this phenomenon, although similar phenomena have long been known by the bead tests used in the analysis of ores and minerals. The bead test is based upon the characteristic ionic colors of metallic oxides dissolved in sodium borate or sodium phosphate. The beads of microcosmic salt containing titanium oxide and iron oxide are dark red. These colors do not arise from either one of the compounds alone.

A systematic study of the above-mentioned phenomena in the future will undoubtedly contribute to a more thorough understanding of them, and will help to formulate a more complete picture of the colored glasses and their chemistry.

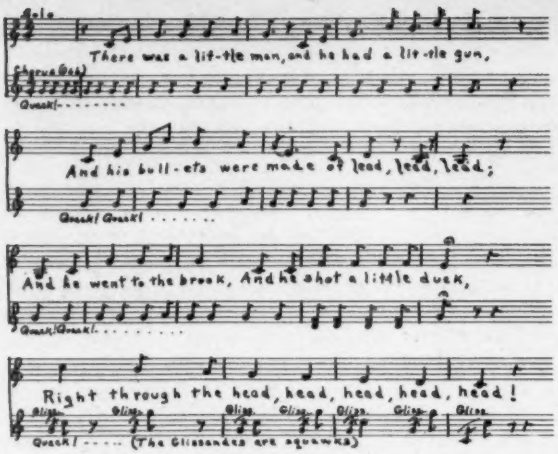
BOOK REVIEW

Lehrbuch der Glastechnik. II. Teil. Die Veredlung des Hohl-und Flachglases. By Professor Bruno Mauder, with Professor Dr. Ing. Ludwig Springer and Dr. F. H. Zschacke. Published by Die Glashutte, Dresden. 280 plus XVI pages, 6 x 8 inches, price, linen-bound, Rm 6.80.

This volume is a companion to the textbook of Glass Technic by Dr. Springer issued from the same source in 1935. It is unfortunate that we have no suitable single word in English which will translate "veredlung", which literally means "ennobling". As applied to hollow-ware, this means cutting, engraving, polishing, painting, decorating, and etching; and as applied to flat glass, particularly rolled plate, it means, in particular, grinding and polishing, together with the cutting of facets, beveling edges, sand blasting, etching, and the making of mirrors, paintings on glass, mosaics, the manufacture of plastic-reinforced or safety glass, and toughened glass.

All of these topics are treated in suitable detail, in authoritative fashion, with 150 illustrations, consisting largely of photographs of products, and photographs of working processes and devices. Many beautiful pieces of ware are depicted, and the method by which the cuttings and decorations are applied is detailed.

The time is undoubtedly right for a book of this kind, presenting modern styles of ornamentation, produced by modern methods. This textbook represents a more advanced treatment than appears in the first volume, which was more definitely a book for young students. This treatise might well be looked through by anyone who is engaged in, or even interested in, any of the processes concerned.

There is an excellent index, and the 30 pages of advertising in the back of the book do not in any way detract from its appearance or its value as a reference work. One is impressed by the frank descriptions of many processes— something which we often fail to get in our own technical literature.—S. R. S.

There was a lit-tle man, and he had a lit-tle gun,
And his bull-ets were made of lead, lead, lead;
And he went to the brook, And he shot a little duck,
Right through the head, head, head, head, head!
(The Glissandos are squawks)

THE LITTLETON ANTHEM

A decided innovation took place in the program of the Glass Division of the A.C.S. when a song, with words and music by Dr. Frank W. Preston, was sung by four of the members with the help of Dr. Navias at the piano. As Dr. Preston remarked, he had a difficult and highly mathematical sort of paper to give, and wanted to introduce it in this lighthearted fashion partly as a relief to the assembly and partly as a tribute to Littleton. A picture of Dr. Littleton was thrown on the screen showing him in his duck-shooting uniform which he is probably wearing even now, as he recuperates at Ft. Pierce, Fla. The words of the song, in so far as they relate to the almost incredible accuracy required in shooting a duck right through the head, have a not-too-remote relationship to the discussion of the probable accuracy of the strength tests determinations, which was the theme of Dr. Preston's paper.

SPODUMENE FOR TOUGH GLASS, TOO

A little-known, little-used mineral, called spodumene, is going to be put to work through a process developed by the U.S. Bureau of Mines, Department of the Interior, for air-conditioning buildings, making of better pottery, and in the production of lithia water, storage batteries, and special types of extremely tough glass. The largest reserves of spodumene are in South Dakota, North Carolina and Maine. Spodumene has heretofore not been used because of the difficulty of separating it from the less valuable minerals; also, there was not a sufficient demand for lithium compounds to permit lower prices.

Technologists at the Nonmetallic Minerals Experiment Station of the Bureau of Mines have now found that the spodumene mineral, if heated in a lime kiln, will be converted to a chalky white mass that can be crumbled between the fingers while all the other minerals present in the ore remain strong. Hence, a gentle mulling, followed by a sifting or the use of a gentle current of air, removes the spodumene from the undesired minerals. It is so simple and easy that it can be carried on in small home-made lime kilns set up by miners or farmers with little technical knowledge. This situation is likely to encourage the production of cheap spodumene.

The fine dust resulting from this treatment is about 80 to 90 per cent pure, and from many localities it will be of acceptable purity. It is much better adapted to use in making lithium chloride than the original hard, dense spodumene. It is also ready to be used in a glass batch, unless nature happened to put magnetic iron minerals in the ore, in which case a preliminary removal of iron minerals would be needed. The pottery makers have desired to use spodumene, but it has been unacceptable because of the fact that at the temperature of a lime kiln it tended to expand and tear pottery to pieces. The *beta* spodumene formed by the heating and now to be sifted out of the heated ore has already been expanded and does not have this disadvantage. Therefore, forget ordinary spodumene and try *beta* spodumene.

Spodumene is the most plentiful of the lithium-bearing ores. It looks much like feldspar and behaves like it. Lithium and lithium salts, heretofore extracted from less common and more expensive ores, now promise to have several important new uses. Lithium chloride solutions, for instance, should find greatly increased use in the conditioning and drying of air in the fast-growing air-conditioning industry.

Further details are given in Report of Investigations 3336, "Beneficiation of Spodumene by Decrepitation," by Oliver C. Ralston and Foster Fraas, copies of which may be obtained from the U. S. Bureau of Mines, Washington, D. C.

MARCH PLATE GLASS PRODUCTION

The production of polished plate glass by member companies of the Plate Glass Manufacturers of America was 20,742,575 square feet in March as compared to 18,676,371 square feet in February, and 16,057,196 square feet produced in March, 1936. This makes a total of 45,791,228 square feet produced in the first quarter of 1937.

WANTED: Upkeep Men and Operators by Pacific Coast factory completely equipped with Lynch R's. High scale paid. Good opportunity.

Address Box 30, THE GLASS INDUSTRY.

EQUIPMENT AND SUPPLIES

NEW PHOTO-ELECTRIC CELL

A photo-electric cell of a new dry-disc self generating type has been introduced by Dr. F. Lowenberg, 10 E. 40th Street, New York, under the trade name, Electrocell. The claimed increase in sensitivity and current output would give more accurate measurements of transparency and light absorption. The sensitivity of these elements is given as 480 microamperes per lumen. They are said to be permanently stable, giving reproducible results, with a broad curve, of relative color sensitivity extending into the field of the ultra-violet. Round models may be obtained in sizes up to 2⅝ inches diameter; rectangular models up to 1½ by 2 inches.

A DIRECTORY OF CHEMISTS

Just received is the new directory of the Association of Consulting Chemists and Chemical Engineers. It contains a complete list of the members of the Association, and in addition a list of the leading consulting firms, the field in which they specialize, and their scope of activities.

PANORAMA OF LUBRICATION

The first three copies of a series, entitled Panorama of Lubrication, has been issued by the Shell Petroleum Corporation, St. Louis, Mo. These booklets give a non-technical discussion of lubrication with diagrams and illustrations. The series to date tells of the sources and refining of oil, the fundamentals of lubrication, and the lubrication of friction type bearings.

Walter S. Aylesworth is now representing The Mullite Refractories Company in the Pittsburgh district, with offices in the Martin Building, in the sale of "Shamva" Mullite super refractories. The company maintains a complete modern research and testing laboratory at the factory in Shelton, Conn.

CATALOGS RECEIVED

Clean Gas Generators. Bulletin No. 95. The Wellman Engineering Co., Cleveland. A new, simplified gas generator is described, giving general design principles, operating data, and operating costs. Well illustrated, including schematics.

Laboratory Microscopes and Accessories. Catalog D-185. Bausch & Lomb Optical Co., Rochester, N. Y. Presenting the specifications of the monocular and binocular microscopes of the Model H series, with accessories, such as condensers and mechanical stages, and various types of microscope lamps. Also included is a table of magnifications and real fields, for both Achromatic and Fluorite objectives. Illustrated.

High Lift Platform Trucks. Elwell-Parker Electric Co., Cleveland. Illustrations show typical applications of the basic machine to various industries. General specifications are also given.

Electric Heating Units and Devices. Catalog GED-650, General Electric Company, Schnectady. Listing numerous small heating units of all kinds, including laboratory and industrial, and various control devices. Specifications given in chart form, with illustrations.

Constant Temperature Laboratory Equipment. Bulletin No. 300. Precision Scientific Co., 1730-32 N. Springfield Ave., Chicago. An 8 page folder giving pictorial and specific description of the company's line of constant temperature laboratory equipment.

Induction Motors. Bulletin No. 1600. Fairbanks, Morse & Co., 600 S. Wabash Ave., Chicago. A description of the company's line of polyphase wound-rotor, or slip-ring, ball-bearing induction motors. These motors have a high starting torque, and a low starting current, and may be operated at a constant, or a regulated variable, speed.

Strip Chart Recording Instruments. Catalogue QEA-1061F. The General Electric Co., Schenectady, N. Y. Describes in detail some improvements in the type CD strip chart recording instruments, for both alternating and direct current, in both portable and stationary models. Also included, are chart specifications and auxiliary equipment.

Fluid Meters. Bulletin No. 31. The Bailey Meter Co., 1050 Ivanhoe Rd., Cleveland. A new 40 page book describing the meters and auxiliary equipment of this company. Schematic diagrams and illustrations are numerous, and many exemplary installations are shown, presenting the manner in which any desired combination of indicating, recording, and integrating features may be combined with a flow mechanism suitable for measurement under high or low pressure.

Lignum-Vitae. Lignum-Vitae Products Co., 96-100 Boyd Ave., Jersey City, N. J. Presents the specifications of lignum-vitae, and offers many suggestions as to its usage.

TAYLOR APPOINTS TWO

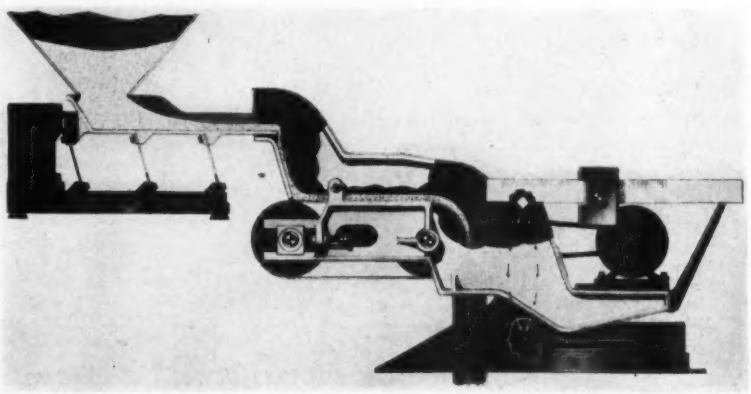
The Chas. Taylor Sons Co., Cincinnati, manufacturers of fire clay and P. B. Sillimanite refractories, has announced the appointment of Robert W. Knauft as sales manager of the Glass House Refractories Division. Mr. Knauft previously represented the company in the Ohio, Indiana, and West Virginia glass manufacturing field. Mr. Edw. L. Bohn, formerly of the North American Refractories Company, has joined the organization as sales manager of the Fire Clay Refractories Division.

NEW PRECISION BATCHING UNIT

A new precision machine applicable to the processes of continuous weigh-feeding, proportioning and batching, called the "Waytrol," is announced by the Jeffrey Manufacturing Co., Columbus, Ohio. This machine combines three features conducive to accuracy: 1. All-electric vibrating feeding; 2. a synchronous weigh-belt on a scale beam so pivoted as to receive material at the most sensitive end; 3. automatic all-electric control sensitized through a device called the Electric Brain.

On this unit feeding and weighing are physically separated processes. Furthermore, the rate of feed to the weigh-belt, which travels at constant speed, is in no way dependent on the volume of material handled, but is governed directly by weight through the Electric Brain, which registers any slight unbalance of the belt, and makes instant correction by speeding up or slowing down the vibrating feeder. For dustless operation and to avoid the possibility of error caused by wind pressure, the entire unit is enclosed in steel and glass. It operates from any standard 60-cycle lighting circuit.

Waytrols are constructed in sizes handling a few pounds up to many tons per hour. The smallest will handle granular material weighing 100 lbs. per cu. ft. at a rate that can be varied from several pounds to a maximum of 4,000 lbs. per hour. All will weigh to within one per cent of absolute at least.



CURRENT PRICES OF GLASS-MAKING MATERIALS

FURNISHED BY PRODUCERS, MANUFACTURERS AND DEALERS

Base Materials

		Carlots	Less Carlots
Barium carbonate ($BaCO_3$), Crude, (Witherite) 90%, 99% through 200 mesh	ton	42.00	45.00
Barium sulphate, in bags	ton	19.00	24.00
Barium sulphate, glassmaker's, carlots, bulk f. o. b. shipping point	ton	15.00-16.00	18.00
Borax ($Na_2B_4O_7 10H_2O$)	lb.	....	....
Granulated	In bags, lb.	.020	.0245-.027
Powdered	In bags, lb.	.0225	.027-.0295
Boric acid (H_3BO_3) granulated	In bags, lb.	.0475	.0525-.055
Calcium phosphate ($Ca_3(PO_4)_2$)	lb.	.07	.07⅛
Cryolite ($Na_3Al\ F_6$) Natural Greenland (Kryolith)	lb.	.08½	.09
Synthetic (Artificial)	lb.	.08½	.09
Feldspar—			
20 mesh	ton	11.00-13.25	
40 mesh	ton	11.50-13.75	
Granular	ton	11.75-14.00	
Semi-granular	ton	11.00-13.25	
L. C. L., (Min. 2 tons) $3.00 per ton additional plus charge for bags			
Fluorspar (CaF_2) domestic, ground, 96-98% (max SiO_2, 2½%)			
Bulk, carloads, f. o. b. mines	ton	31.50	....
In bags	ton	33.10	38.00-40.60
Kryolith (see Cryolite)			
Lead Oxide (Pb_3O_4) (red lead) (N. Y.)	lb.	.085	10¼
In 5 Ton lots	lb.	....	.09
Less than 5 Tons	lb.	....	.0 95
Lime—			
Hydrated ($Ca(OH)_2$) (in paper sacks)	ton	10.50	....
Burnt (CaO) ground, in bulk	ton	7.00	....
Burnt, ground, in paper sacks	ton	9.00	....
Burnt, ground, in 280 lb. bbls	Per bbl.	2.25	2.25
Calcined (K_2CO_3) 96-98%	lb.	.065-.0675	.07¾
Hydrated 80-85%	lb.	.055	.0575
Salt cake, glassmakers (Na_2SO_4)	ton	18.00	27.00
Soda ash (Na_2CO_3) dense, 58%—			
Bulk	Flat Per 100 lb	95	....
In barrels	Per 100 lb.	1.35	....
In bags	Per 100 lb.	1.10	....
Sodium nitrate ($NaNO_3$)—			
Refined (gran.) in bbls	Per 100 lb.	....	2.25-2.65
95% and 97%			
Bulk	Per 100 lb.	1.275	....
200 lb. bags		1.34	1.39
100 lb. bags		1.375	1.425

Special Materials

		Carlots	Less Carlots
Aluminum hydrate ($Al(OH)_3$)	lb.	....	.03½
Aluminum oxide (Al_2O_3)	lb.	.04	.05
Antimony oxide (Sb_2O_3)	lb.	....	.16¾
Arsenic trioxide (As_2O_3) (dense white) 99%	lb.	.03	.03¾
Barium nitrate ($Ba(NO_3)_2$)	lb.	....	.07¾
Rutile (TiO_2) powdered, 95%	lb.	.10-.12	.13-.15
Sodium fluosilicate (Na_2SiF_6)	lb.	.06½	.07
Tin Oxide (SnO_2) in bbls	lb.	....	.60
Zinc Oxide (ZnO)			
American process, Bags	lb.	.06	.06¼
White Seal, 150 lb. bbls	lb.	.08¼	.08½
Green Seal bags	lb.	.07½	.07¾
Domestic White Seal bags	lb.	.08	.08¼
Red Seal, bags	lb.	.07	.07¼
Zircon			
Granular (Milled .005-.02c higher)		.07	.07½-.08
Crude, Gran. (Milled .005-.02c higher)		.03½	.04-.05

Coloring Materials

		Carlots	Less Carlots
Barium selenite ($BaSeO_3$)	lb.	....	1.50-1.75
(Commercial, 25% Selenium)	lb.	....	.90
Cadmium sulphide (CdS)	lb.	....	.90-1.05-1.10
Chromite	lb.	....	.0215
Cerium hydrate			
100 lb. drums and 600 lb. barrels	lb.	....	.60
Chrome Oxide Green, 400 lb. bbls.	lb.	....	.22-.26
Cobalt oxide (Co_2O_3)			
In bbls	lb.	....	1.41
In 10 lb. tins	lb.	....	1.51
Copper oxide			
Red (Cu_2O)	lb.	....	.20¼
Black (CuO)	lb.	....	.18½-20¼
Black prepared	lb.	....	.22
Iron Oxide—			
Red (Fe_2O_3)	lb.	....	.0425
Black (Fe_3O_4)	lb.	.04½	....
Iron Chromate	lb.	....	.035-.05
Lead Chromate ($PbCrO_4$)	lb.	....	.16
Manganese, Black Oxide			
In Paper bags	ton	50.00	53.00-58.00
In Burlap bags	ton	52.00	55.00-60.00
In Casks	ton	54.00	57.00-62.00
Neodymium oxalate, 50 lb. drums	lb.	....	3.00
Nickel oxide (Ni_2O_3), black	lb.	....	.35-.40
Nickel monoxide (NiO), green	lb.	....	.35-.40
Potassium bichromate ($K_2Cr_2O_7$)—			
Crystals	lb.	....	.08⅝
Powdered	lb.	....	.09½
Potassium Chromate (K_2CrO_4) 100 lb. kegs	lb.	....	.27
Powder blue	lb.	....	.18¾-.19¾
Rare earth hydrate			
100 lb. drums	lb.	....	.35
325 lb. barrels	lb.	....	.30
Selenium (Se) In 100 lb. lots	lb.	....	2.00
In lesser quantities	lb.	....	2.10
Sodium bichromate ($Na_2Cr_2O_7$)	lb.	.06⅝	.07
Sodium chromate (Na_2CrO_4) Anhydrous	lb.	....	.08⅜
Sodium selenite (Na_2SeO_3)	lb.	....	1.80-2.00
Sodium uranate (Na_2UO_4) Orange	lb.	....	1.50-1.55
Yellow	lb.	....	1.50-1.55
Sodium uranyl carbonate	lb.	....	.80-.90
Sulphur (S)—			
Flowers, in bbls	Per 100 lb.	3.35	3.70-4.10
Flowers, in bags	Per 100 lb.	3.00	3.35-3.75
Flour, heavy, in 250 lb. bbls	Per 100 lb.	2.90	3.25-3.65
Uranium oxide (UO_2) (black, 96% U_3O_8) 100 lb. lots. Black	lb.	....	2.25
Yellow orange	lb.	....	1.50

Polishing Materials

		Carlots	Less Carlots
Emery, Turkish	lb.	....	.07
Pumice Stone,			
American Ground Italian FFF, FF, F	lb.	....	.03
0, 0½, ½, 1.	lb.	....	.03¾
Putty Powder	lb.	....	.38-.42
Rotten Stone	lb.	....	.03
Rouge, Red	lb.	....	.14
Black	lb.	....	.16